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# STUDY OF UTILIZATION AND DISPOSAL OF LIME SLUDGES CONTAINING PHOSPHATES

R. E. Opferkuch, et al

Monsanto Research Corporation

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# STUDY OF UTILIZATION AND DISPOSAL OF LIME SLUDGES CONTAINING PHOSPHATES

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Preliminary cost estimates are presented for several levels of process complexity in liming secondary effluent with potential recovery of lime and phosphate. A summary of transportation costs, by various means, for removal of sludge from the treatment plant site is also presented.

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# SECTION I

## CONCLUSIONS

1. For agricultural use, sludge derived from tertiary sewage treatment for phosphate removal requires essentially no processing, but has essentially no value compared with commercial aglime, or agrock, and commercial fertilizers. To utilize significant amounts of sludge for agricultural purposes, it would essentially have to be given away.

2. The cost of processing to prepare a suitable product for the phosphate industry (based on phosphate content alone) far exceeds the value of the product.

3. Potential recovery of the more valuable magnesium, if the production capacity is great enough, could result in favorable economics.

4. There is an intrinsic deterrent to chemical conversion of sludge for utilization in that, for very practical reasons, most municipal treatment plants do not desire the additional operation of a chemical process plant and the associated marketing problems.

## SECTION II

## RECOMMENDATIONS

1. The economics of magnesium recovery from tertiary lime sludges should be explored.

2. Since there is some inherent value in the sludge for soil sweetening and in the form of available phosphate and possibly other desirable trace minerals, a study is warranted of: means for promoting user acceptance of the sludge (dry, calcined); those areas where sludge can be disposed of by this agricultural method; and, means of distribution or "marketing."

3. A reasonable alternative might well be the establishment of a central plant that would use as raw material sludge from a number of municipal sewage treatment plants, and process it for recovery of several chemical values in quantities that would make production economical and permit a satisfactory return on capital.



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## SECTION III

## INTRODUCTION

The addition of lime to the effluent from secondary sewage treatment can quite effectively remove soluble phosphates by precipitating them as the insoluble calcium salts (Ref. 1). Such treatment also removes hardness, some residual organic matter, and other diverse minerals by precipitation and/or adsorption. Thus a fairly high quality water is possible. Also, a considerable amount of sludge is generated. The precipitate, or sludge, formed contains a variety of materials most common of which are:

$$Ca_3(PO_4)_2$$

$$CaCO_3\text{-}Ca(OH)_2$$

$$Mg(OH)_2$$

The question is: What to do with the sludge? It is premature to say that there is a "standard liming process" since development of liming processes is currently continuing. Both the method of operation and the character of secondary effluent treated affect the quantity and composition of the sludge produced.

In most cases, however, excess lime, i.e., well above stoichiometric, is required to achieve the high pH (about 11) at which precipitation is most effective. Hence, one is faced with the decision whether to recover lime or not. There are many factors affecting the decision and it may well be that practice of lime recovery will not fit all circumstances.

In the long run, the problem is still there, whether lime is recovered or not. Recovery only affects the composition of the sludge because of the recycling and buildup of inerts at the expense of active lime.

Thus, it is not practical to define a "standard sludge" although, in general, the system producing it might resemble that shown schematically in Figure 1.



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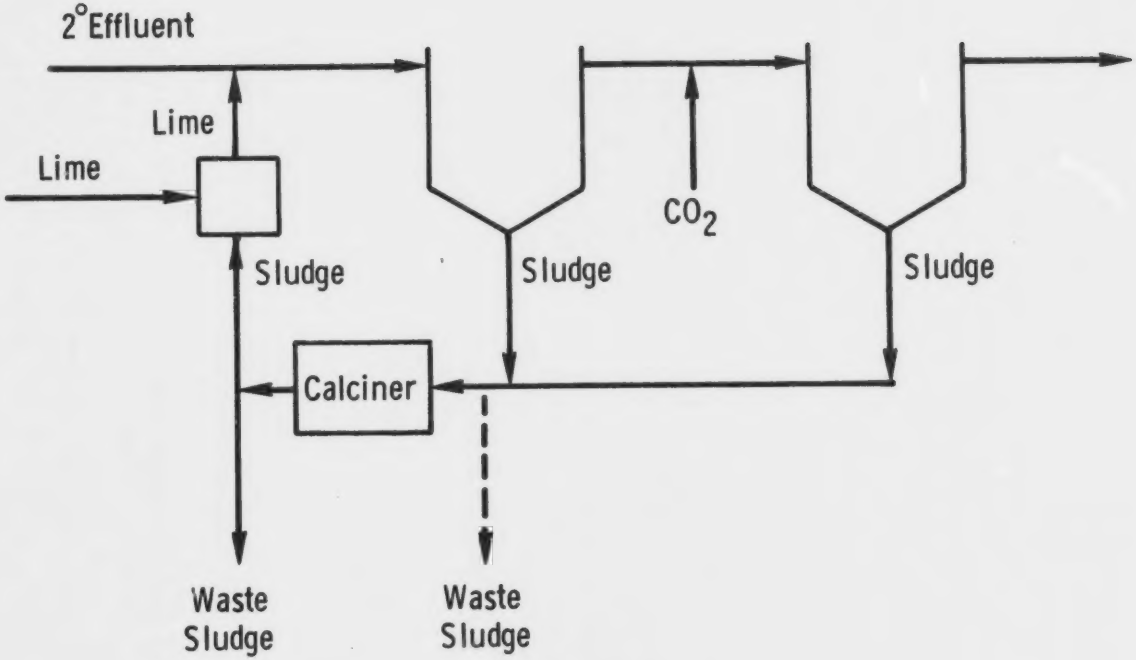


Figure 1. Lime Treatment for Phosphate Removal

If we assume recovery of lime, we have the option of wasting wet sludge (cake) or calcined sludge, depending upon the method of use or disposal. This brings us to the subject: What potential uses does the sludge have?

The answer lies, in part, in the sludge composition, the variability of which is exemplified by the composition range observed for typical calcined sludge:

| | |
|---|---|
| $Ca_3(PO_4)_2$ | 8-40% |
| CaO | 20-75% |
| MgO | 1-60% |
| Other | 0-13% |

When one reviews the products in which this combination of materials exists, though not necessarily in these ratios, a list of potential product areas emerges in which these materials appear, Table 1.

Table 1

POTENTIAL USES OF LIME/PHOSPHATE SLUDGE

A. DISPOSAL OF PHOSPHATE SLUDGE IN AGRICULTURAL PRODUCTS "AS IS"

1. Phosphate Lime
2. "Sweet Manure"

B. CHEMICAL CONVERSION OF PHOSPHATE SLUDGE

1. Conversion to Phosphoric Acid
2. Triple Superphosphate Manufacture
3. Ammonium Phosphate Fertilizers

C. BUILDING PRODUCTS

1. Plasters and Refractories
2. Cement
3. Glass Construction Material

Some of the major factors that have to be considered in evaluating potential uses of sludge are these:

1. Availability and cost of alternative means of disposal.

2. Amount of on-site processing and relevance to treatment plant operations.

3. Required R&D effort to attain process and product.

4. Product market potential.

The potential market evaluation for a proposed product has many facets, the major ones being:

4. Product market potential

   a. Cost of production versus selling price

   b. Share of market

   c. Minimum economic production

   d. Effect on market

   e. Mode of distribution

   f. Market structure

   g. Past and current market growth trends

In applying all these considerations to our list of potential products, we rather quickly eliminated the items under the last heading in Table 1 on the basis of R&D costs and numerous marketing complications. In Category B, potential depends largely upon the $P_2O_5$ content of the product sludge. Since the competition is phosphate rock, the sludge must offer certain advantages in order to be used as raw material in phosphate conversion.

The applications noted in Category A appear to require a minimum of processing and likely could be handled at the treatment plant without difficulty. A product like "sweet manure" is analogous, but not identical, to a product like Milorganite, or compost, with the minor added, though questionable, potential benefit of the sludge components. Similarly, a product such as "phosphate lime" is analogous to aglime, or agrock, yet without really having the sweeting value per unit weight, i.e., it would not compete cost-effectively.

A comparison of the composition of phosphate-lime sludge with that of natural phosphate rock, or ore, is revealing.

Table 2

COMPOSITION AND COST OF PHOSPHATE ORE

| BPL* | % $P_2O_5$ (avg) | (10/31/69) $/ton |
|---|---|---|
| 66-68 | 30.7 | 6.50 |
| 68-70 | 31.6 | 7.50 |
| 70-72 | 32.5 | 8.15 |
| 74-75 | 34.1 | 9.20 |
| 76-77 | 34.8 | 10.20 |

*BPL = bone phosphate of lime value, which is equivalent to the $Ca_3(PO_4)_2$ content

Table 2 shows the range of $P_2O_5$ content and corresponding prices of commercial natural rock at the mine. It can be seen that in order for lime-phosphate sludge to be competitive, the calcium phosphate content must be above 65%.

To begin talking about sludge phosphate content requires at once some definitions and assumptions. First, it is assumed the feed, i.e., the secondary effluent, contains 25 mg/l $PO_4$ and it is defined that 400 mg/l of lime will be added to remove it. The residual $PO_4$ in the limed effluent will be defined as less than 1 mg/l. It is further assumed that the sludge will consist only of tricalcium phosphate and calcium carbonate. Also, the sludge will be calcined and recycled, with make-up lime added each cycle to maintain 400 mg/l dose. In other words, the calcium phosphate content gradually builds up as it recycles around the system. The growth in calcium phosphate under these ideal conditions follows the curve shown in Figure 2.

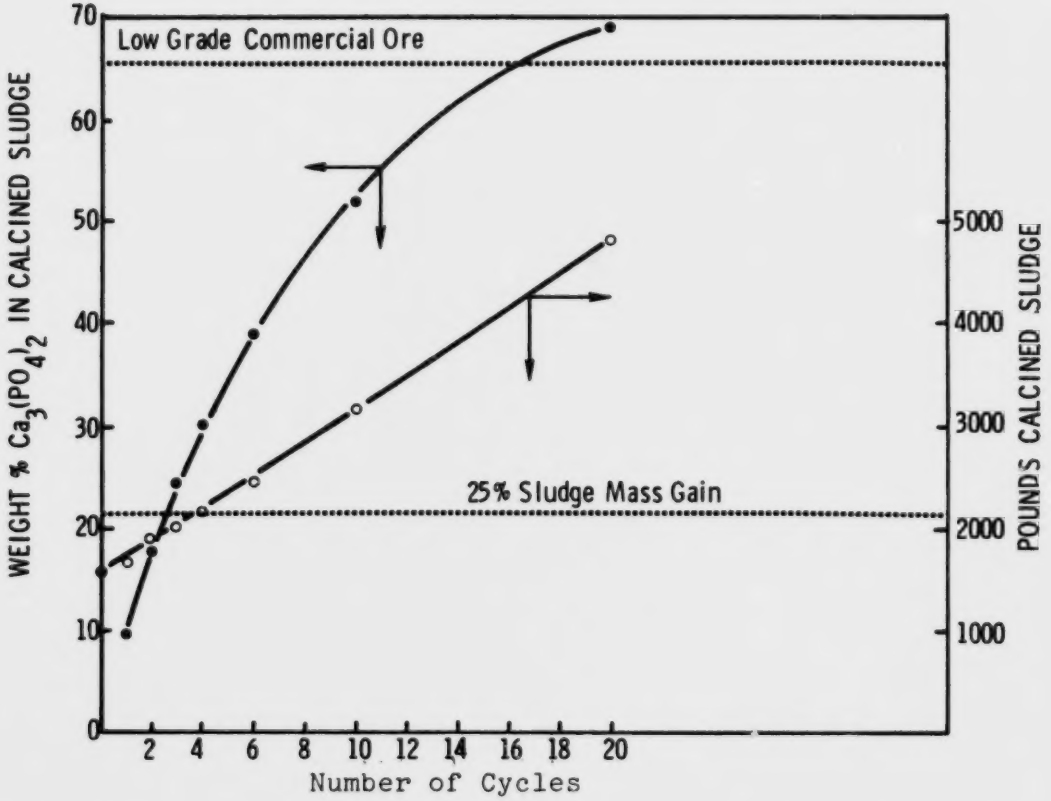


Figure 2. Change in Calcined Sludge Character During Recycle

From this, it appears that after 18-20 cycles, the phosphate content is into the commercial range. The sludge mass, however, has almost tripled. If a sludge mass increase of 25% is allowed, phosphate content drops to about 20%. Further, real sludge contains other material besides just tricalcium phosphate and calcium carbonate, so that, in practice, less than 20% phosphate content would be expected for the 25% sludge mass increase, and the feed/dosage level picked.

The question immediately arises: How can one beneficiate, or enrich, this material? Natural rock contains clay, quartz, limestone, and sometimes, dolamite. Methods that have been studied for beneficiating phosphate ore, in addition to hydraulic beneficiation, are: flotation in various types and densities of liquids, and thermal beneficiation.

It must be recognized that the problem with phosphate sludge may be entirely different because it is a manufactured product and the surface characteristics, particle size, densities and other relevant properties will depend on the process. Further, of two potential approaches, flotation was rejected since it employed organics such as sodium oleate, napthenic amine, and other amines in the $C_{16-20}$ range and was considered too complex. Thermal treatment, however, was considered as a potential method for beneficiation and is described below.

The objective, then, of the program condenses to: (1) means of useful disposal of the sludge, through beneficial application of the whole sludge or recovery of a useful constituent, and (2) disposal of the sludge through removal from the site.

The ultimate solution to the problem is indicated to be an economic solution. From the view of useful product recovery, marketing of the product assumes importance. Thus, in the following, the aspects of useful product recovery and market potential are considered as well as the economics of merely removing the material from the site. Some laboratory work was undertaken to provide a basis for predicting the potential of useful product recovery in relation to market potential for such product.

## SECTION IV

## MARKET ASPECTS OF SLUDGE DISPOSAL

The market outlook for phosphate sludge and the products into which it might be converted was discussed with members of Monsanto Company's Inorganic Division Sales Department. The consensus was that a high grade calcium phosphate represents the most valuable product; that is, it is optimum between product value and the amount of on-site processing required, including the generation and disposal of waste streams during processing.

It was stated that the outlook for the sludge, as is, in agricultural outlets is very poor. Admittedly, in some specific locations desirable arrangements might be developed for a product such as "sweet manure" or phosphate lime, but as a universal solution to disposal, such outlets would be considered very unattractive.

### PHOSPHATE ROCK

The estimated consumption of $P_2O_5$ plant nutrient in the U.S. for the period 1966 to 1980 is shown in Table 3 (Ref. 3).

Table 3

ESTIMATED CONSUMPTION OF $P_2O_5$ PLANT NUTRIENT

| Year | Short Tons (millions) |
|---|---|
| 1966 | 3.9 |
| 1970 | 5.5 |
| 1980 | 6.3 |

By comparison, the total "recoverable" sewage output from the nation has been estimated at 14 billion gallons per day, and the output from one source alone, Chicago, at 1.3 bgd. Assuming an average of 10 mg/l of phosphorus in the effluent, the respective equivalent $P_2O_5$ quantities available in sewage effluent are 487,000 short tons/yr for the nation as a whole, and 45,000 short tons/yr for Chicago alone. Thus, potentially, roughly 10% of the plant nutrient $P_2O_5$ market could be supplied by phosphate recovered from sewage effluent. Furthermore, about 65% of the estimated



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growth in consumption of this plant nutrient will occur in the midwestern and southwestern states (Ref. 3). Therefore, it appears that a high quality phosphate "rock" produced in adjacent regions would, because of its purity and freight advantages, find a ready outlet among phosphate rock users. Figure 3 shows the estimated value of high quality phosphate based on the extrapolation of prices for Florida rock of various qualities.

The concept of converting the phosphate to phosphoric acid, ammonium phosphate or a superphosphate for agricultural uses, while certainly technically feasible, does not appear attractive overall because of the additional processing which would be required at the treatment plant site and the complex marketing problems which would arise. In isolated cases, where a market for one of these products, in relatively small quantities, could be assured, it may be desirable to convert the phosphate at the treatment plant site. Again, beneficiation of the sludge would play an important part in process and product economics, but it would be far simpler to stop at the point of obtaining a relatively pure calcium phosphate and market this more versatile product to the phosphate industry.

Wet-process phosphoric acid producers are primary users of phosphate rock. Owing to a trend toward high analysis phosphate fertilizers such as triple superphosphates and ammonium phosphate, which are made from wet-process phosphoric acid, the production of this acid, which was 3,530,000 tons (as $P_2O_5$) in 1966, is expected to double over the next 10 years (Ref. 4). Table 4 lists the wet-process phosphoric acid plants in the United States. Figure 4 shows that the plants are well scattered throughout the country, and a high-quality phosphate sludge from big metropolitan areas in the north, east, and central parts of the country would find a ready outlet to these plants.

Florida produces about 70% of the nation's phosphate rock and 50% of the wet-process phosphoric acid. However, the nation's two largest $P_2O_5$ consuming areas are the East North Central (region IV, Figure 2) and the West North Central (region V, Figure 2; see also Table 5) with annual consumption in 1967 of 1,198,000 and 1,101,000 tons of $P_2O_5$, respectively, or approximately 54% of the nation's total $P_2O_5$ consumption. Furthermore, about 65% of the estimated growth in consumption of this plant nutrient is expected to occur in these regions (Ref. 3). It seems likely, therefore, that the phosphate fertilizer

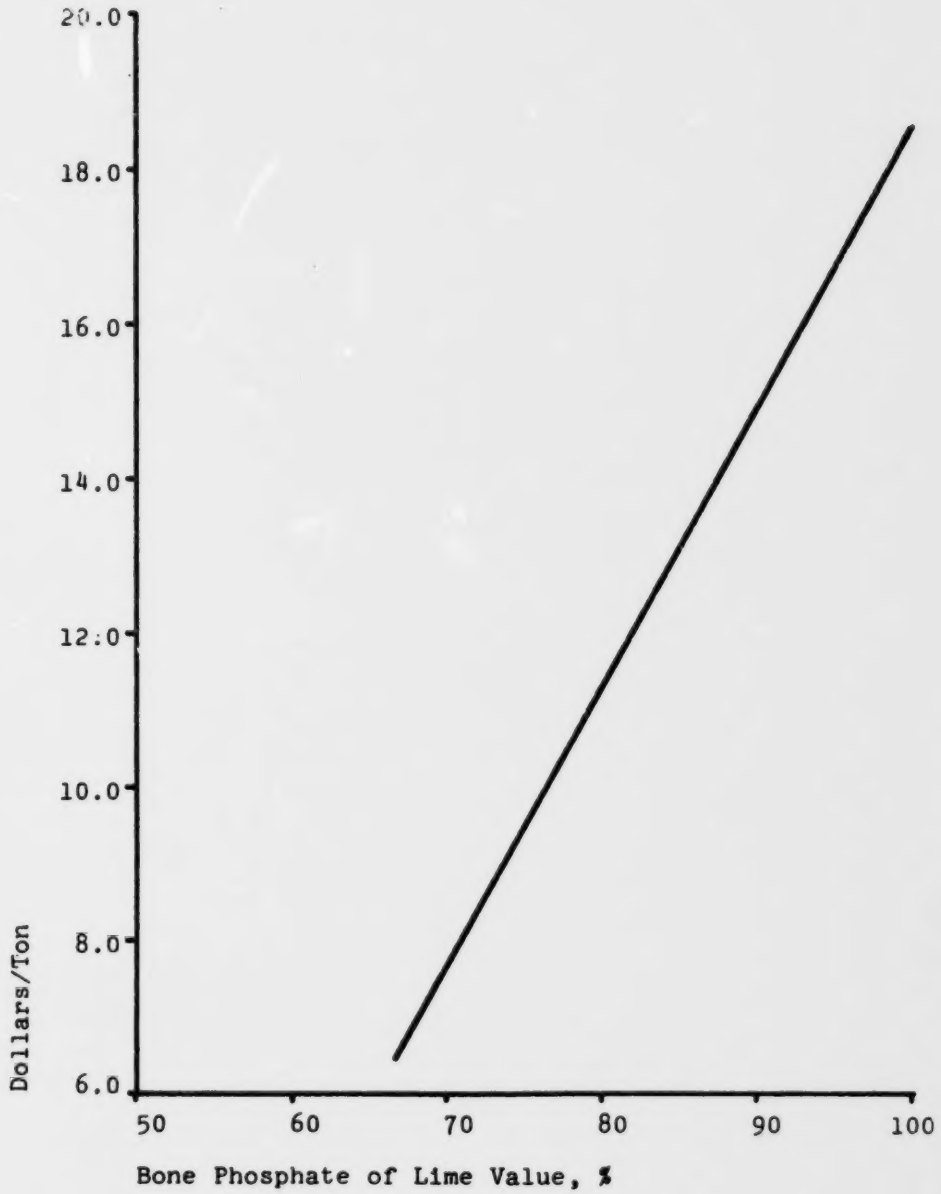



Figure 3. Extrapolated Value of Pure "Phosphate Rock" (from *Oil, Paint and Drug Reporter*, 8/5/69)

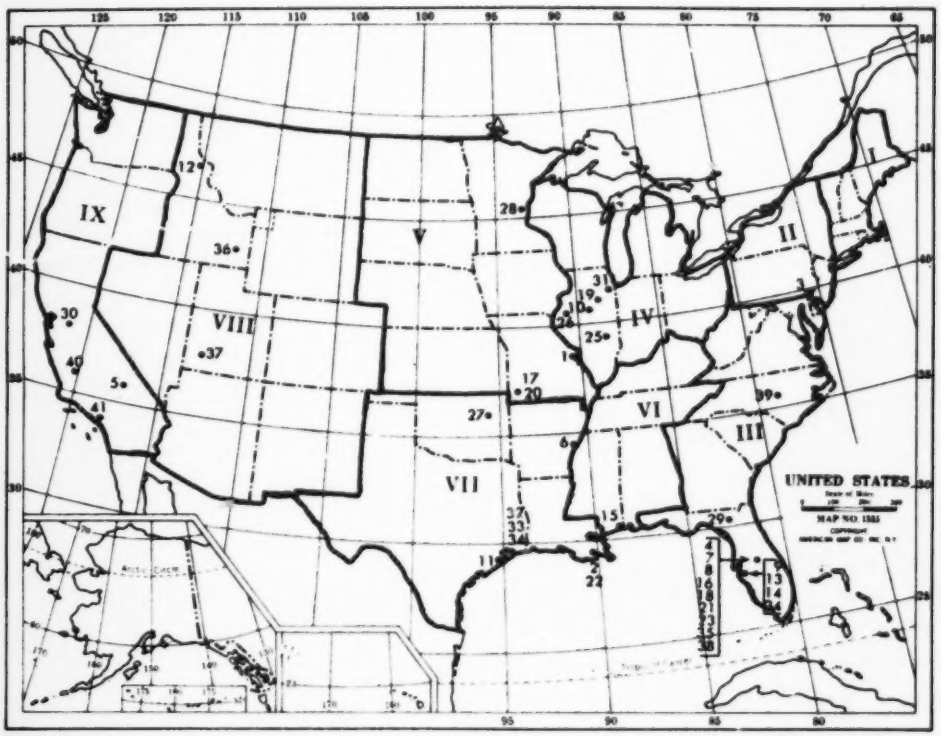



Figure 4. Wet Process Phosphoric Acid Manufacturing Plants (Ref. 6) and Farm Areas Designated by U.S. Department of Agriculture

Pacific Area (IX) includes Alaska and Hawaii

## Table 4

## WET-PROCESS PHOSPHORIC ACID PLANTS IN THE UNITED STATES, PLANNED EXPANSIONS, AND NEW PLANTS UNDER CONSTRUCTION (REF. 6)

| Company | Location* | Capacity July 1, 1965 | Planned Additional Capacity 1965 | 1966 | 1967 |
|---|---|---|---|---|---|
| | | | (Thousand Short Tons of $P_2O_5$/Yr.) | | |
| Allied Chemical Company | East St. Louis Ill.(1) | 50 | ---- | ---- | ---- |
| | Geismar, Louisiana (2) | -- | ---- | ---- | 100 |
| | North Claymont, Del.(3) | 35 | ---- | ---- | ---- |
| American Cyanamid Company | Brewster, Fla. (4) | 200 | ---- | ---- | ---- |
| American Potash and Chemical Co. | Trona, California (5) | 5 | ---- | ---- | ---- |
| Arkla Chemical Company | Helena, Arkansas (6) | -- | N.A. | ---- | ---- |
| Armour Agricultural Chemical Co. | Barlow, Florida (7) | 85 | ---- | ---- | ---- |
| | Ft. Meade, Florida (8) | 190 | ---- | ---- | ---- |
| Borden Chemical Company | Port Manatee, Florida (9) | -- | ---- | 76 | ---- |
| (Smith-Douglass Company) | Streator, Illinois (10) | 33 | ---- | ---- | ---- |
| | Texas City, Texas (11) | 40 | ---- | ---- | ---- |
| Bunker Hill Company | Kellogg, Idaho (12) | 33 | N.A. | ---- | ---- |
| Central Phosphates, Inc. | Plant City, Florida (13) | -- | 200 | ---- | ---- |
| Cities Service Oil Company (Tennessee Corporation) | Tampa, Florida (14) | 340 | N.A. | ---- | ---- |
| Coastal Chemical Company | Pascagoula, Miss. (15) | 45 | 90 | ---- | ---- |
| Consumers Cooperative Association | Lakeland, Florida (16) | -- | 200 | ---- | ---- |
| (Farmers Chemical Co.) | Joplin, Missouri (17) | 53 | ---- | ---- | ---- |
| Continental Oil Company (American Agricultural Chemical Co.) | Pierce, Florida (18)] | -- | 200 | ---- | ---- |
| Des Plaines Chemical Company | Morris, Illinois(19) | 50 | ---- | ---- | ---- |
| W. R. Grace and Company | Joplin, Missouri (20) | 33 | ---- | ---- | ---- |
| | Ridgewood, Florida (21) | 165 | ---- | 100 | ---- |
| Hooker Chemical Co. | Taft, Louisianna (22) | 200 | ---- | ---- | ---- |
| International Minerals & Chemical Co. | Bonnie, Florida (23) | 490 | ---- | ---- | ---- |
| Mobil Chemical Co. | Nichols, Florida (24) | 150 | N.A. | ---- | ---- |
| National Distillers and Chemical Co. | Tuscola, Illinois (25) | 30 | ---- | ---- | ---- |
| New Jersey Zinc Corporation | Depue, Illinois (26) | -- | ---- | 125 | ---- |
| Nipak, Inc. | Tulsa, Oklahoma (27) | 30 | ---- | ---- | ---- |
| Northwest Coop. Mills, Inc. | Pine Bend, Minn. (28) | 40 | ---- | ---- | ---- |
| Occidental Agricultural Corp. | White Springs, Florida (29) | -- | ---- | 175 | ---- |
| (Best Fertilizer Co.) | Lathrop, California (30) | 20 | ---- | ---- | ---- |
| Olin Mathieson Chemical Co. | Joliet, Illinois (31) | 125 | ---- | ---- | ---- |
| | Pasadena, Texas (32) | 123 | 210[a] | ---- | ---- |
| Phillips Chemical Company | Pasadena, Texas (33) | 60 | ---- | ---- | ---- |
| Phosphate Chemicals, Inc. | Houston, Texas (34) | -- | 100 | ---- | ---- |
| Royster Chemical Co. | Mulberry, Florida (35) | 30 | ---- | ---- | ---- |
| J. R. Simplot Company | Pocatello, Idaho (36) | 120 | 120 | ---- | ---- |
| Stauffer Chemical Company | Garfield, Utah (37) | 50 | 50 | ---- | 100 |
| Swift & Company | Agricola, Florida (38) | 90 | ---- | ---- | ---- |
| Texas Gulf Sulphur Corp. | Lee Creek, N. C. (39) | -- | ---- | 350 | ---- |
| Valley Nitrogen Producers, Inc. | Helm, California (40) | 60 | ---- | ---- | ---- |
| Western States Chemical Company | Dominguez, Calif. (41) | 12 | ---- | ---- | ---- |
| TOTAL ANNOUNCED CAPACITY..... | | 3097 | 4254 | 5080 | 5280 |

[a]Will replace existing facilities

*Numbers in parentheses are keys to location on Figure 4.

Table 5

U.S. FERTILIZER CONSUMPTION (REF. 5)

Primary Plant Nutrients

Thousands of Tons

| | Area | Nitrogen 1966 | Nitrogen 1967 | $P_2O_5$ 1966 | $P_2O_5$ 1967 | $K_2O$ 1966 | $K_2O$ 1967 | Total 1966 | Total 1967 |
|---|---|---|---|---|---|---|---|---|---|
| I | New England | 45 | 44 | 52 | 50 | 50 | 47 | 147 | 141 |
| II | Middle Atlantic | 205 | 217 | 256 | 254 | 238 | 230 | 699 | 701 |
| III | South Atlantic | 629 | 687 | 512 | 533 | 688 | 732 | 1828 | 1953 |
| IV | East North Central | 1175 | 1308 | 1082 | 1198 | 1158 | 1296 | 3414 | 3803 |
| V | West North Central | 1345 | 1655 | 939 | 1101 | 462 | 653 | 2746 | 3409 |
| VI | East South Central | 417 | 452 | 327 | 342 | 338 | 353 | 1082 | 1147 |
| VII | West South Central | 668 | 725 | 347 | 386 | 170 | 191 | 1185 | 1302 |
| VIII | Mountain | 241 | 275 | 163 | 186 | 9 | 13 | 414 | 474 |
| IX | Pacific | 549 | 609 | 195 | 228 | 59 | 80 | 802 | 918 |
| | TOTAL. . . . . | 5273 | 5974 | 3873 | 4279 | 3172 | 3596 | 12,318 | 13,851 |

Table 6

POSSIBLE 1985 WORLD PHOSPHATE ROCK RESERVES.
BASES: 70 BPL ROCK AND GREATER. PRODUCTION COSTS RELATIVELY SIMILAR TO PRESENT LEVELS.
PUBLISHED, ESTIMATED KNOWN RESERVES (REF. 7).
(MILLIONS OF METRIC TONS, ORDER OF MAGNITUDE)

| | Cumulative Production to 1985 | Reserves by 1985 |
|---|---|---|
| U.S. | | |
| Florida (pebble) | 600 | Largely depleted |
| Other eastern U.S. | 100 | 300 |
| Western U.S. | 90 | 100 |
| Tennessee | 40 | Depleted |
| Other | 90 | 70 |
| Africa | | |
| Morocco | 380 | Considerably depleted |
| Other North Africa | 250 | 800 |
| Spanish Sahara | 100(?) | 1100(?) |
| Uganda | ? | ? |
| Other | 150 | 150 |
| South America | 100 | 130 |
| U.S.S.R. | 500 | 1000 |
| China | 100 | Largely depleted |
| Other* | 300 | Mostly depleted |
| | 2800 | 3750 (say) |

*Not including large deposites recently found in Queensland, Australia

industry will expand in these areas, particularly if a high-quality rock is available. It is a happy coincidence that these areas either include, or are adjacent to, the densely populated New England, Middle Atlantic, and East North Central regions (I, II, and IV, Figure 2) from which the largest supply of sewage-derived phosphate "rock" is expected. Thus, a high-quality phosphate from this source would be competitive with Florida rock from the standpoints both of quality and transportation cost.

It has been estimated that the average annual compounded growth rate for consumption of $P_2O_5$ nutrient from 1970 to 1980 will be about 3% (Ref. 3). At the present rate of phosphate rock demand most of the U.S. reserve of high-grade rock will be virtually depleted by 1985 (Table 6). New sources of $P_2O_5$ nutrient will be badly needed. Considering this, it seems that a high grade phosphate "rock" derived from sewage effluent could play an important role in supplying part of the raw material for the phosphate fertilizer industry.

## AGRICULTURAL LIME

A market review of limestone and lime for agricultural use was made. It appears that it may be possible to sell phosphate lime sludge for this application. "Aglime" is any compound of calcium, or calcium and magnesium, which when added to soils, will neutralize soil acidity. Most agronomists agree that a pH of between 6.5 and 7.0 is right for greatest availability of nutrients (Ref. 8).

Table 7 shows the sales of aglime in the United States. Within the last few years "agstone" has largely replaced lime, because its precipitation is slower in rate and more evenly spread throughout the soil, thus maintaining potency in the soil longer than lime. Agstone, therefore, requires less frequent application; it is also cheaper and easier to handle than lime. The principal advantage of lime over limestone is its ability to neutralize soil acids faster. It has higher neutralizing value per ton. Nevertheless, limestone is sufficiently cheaper so that it has higher neutralizing value per dollar.

Prices for aglime fluctuate according to demand, type, and source of supply. The purity of agricultural limestone is relatively unimportant, since any calcareous material, including impure marls, can be utilized successfully in improving soil tilth, providing a sufficient quantity is

Table 7

SALES OF AGRICULTURAL LIME IN THE UNITED STATES, 1964-1966 (REF. 9)

| Item | Quantity | | | Value | | |
|---|---|---|---|---|---|---|
| | 1954 | 1965 | 1966 | 1964 | 1965 | 1966 |
| | Tons | Tons | Tons | Dollars | Dollars | Dollars |
| Agricultural lime and liming material sold by producers: | | | | | | |
| Lime from limestone: | | | | | | |
| Quicklime[1] | 87,015 | 93,171 | 93,747 | 2,616,972[2] | 2,422,576[2] | 2,2:9,904[2] |
| Hydrated | 113,435 | 81,492 | 74,294 | --- | --- | --- |
| Limestone pulverized | 26,791,000 | 28,289,000 | 30,080,000 | 46,147,000 | 48,586,000 | 52,378,000 |
| Calcareous Marl | 228,000 | 219,000 | 224,000 | 156,000 | 150,000 | 154,000 |

[1]Lime from oyster shells included with quicklime from limestone

[2]Value not quoted separately

used. While there is no universally established procedure for purchasing limestone, the trend is to buy it on an equivalent calcium oxide basis, because the combined calcium oxide and magnesium oxide content determines the neutralizing power of any calcareous material (Ref. 10). Since agronomists have discovered that many soils have a deficiency in magnesium, higher content of magnesium oxide could bring a higher price. Particle size of the ground limestone is an important factor. However, agronomists are not united in their opinion on the proper size of limestone to recommend to farmers. In the middle west, coarse limestone (10-mesh size) is preferred, while in the east and in many southern states ground limestone (50- up to 200-mesh size) is recommended (Ref. 10).

The average price of $1.74 per ton of agricultural limestone reported in 1966 represents an increase of only 14 percent over 1948. The price of agricultural lime in 1949 was about $10.79 per ton and today is $15.50 per ton (Ref. 11). The relatively stable price of aglime does not reflect a lessening of demand, but rather increased efficiencies in production and transportation. It must be mentioned that in connection with pricing for liming consumption, about 70 percent of the liming materials consumed at present receive some form of Federal cost-sharing. In some of the less prosperous agricultural states, 85 percent Federal participation is involved. Federal subsidies make pricing complicated. If a state employs its soil conservation funds for other approved services, liming consumption sharply declines. Federal funds available to farmers for soil conservation have dwindled from approximately $420 million 30 years ago to about $222 million in 1964.

Table 8 shows the sectional agricultural limestone usage in the United States. Figure 5 indicates the increase in limestone usage between 1954 and 1966. This increase is not nearly enough to meet the need. Agronomists have estimated that 80 million tons of lime are needed annually for proper soil pH. Yet only 30 million tons were used in 1966 (Ref. 8). This figure represents only 38 percent of estimated needs. Table 9 shows the limestone consumption and the percent of estimated needs.

In a recent field trial jointly performed by the University of Illinois and Southern Illinois University, the importance of limestone was demonstrated. Soil treated with lime produced an increase of 26 percent in corn yield and an increase of 64 percent in yield of soybeans at 7.2 pH level (Ref. 8). Agronomists are well aware of advantages derived

Table 8

SECTIONAL AGRICULTURAL LIMESTONE USAGE (REF. 8)

(shown in 1000 tons)

| Year | Southern | Northeastern | East Central | North Central | Western |
|---|---|---|---|---|---|
| 1954 | 1,766 | 1,877 | 2,959 | 12,259 | 969 |
| 1955 | 1,811 | 2,099 | 3,202 | 13,376 | 787 |
| 1856 | 2,200 | 2,171 | 3,453 | 13,648 | 696 |
| 1957 | 2,018 | 2,052 | 3,391 | 13,572 | 748 |
| 1958 | 2,358 | 2,114 | 3,418 | 14,1-6 | 714 |
| 1959 | 2,836 | 2,395 | 4,349 | 12,357 | 734 |
| 1960 | 2,817 | 2,405 | 4,362 | 12,780 | 690 |
| 1961 | 3,058 | 2,151 | 4,547 | 12,076 | 607 |
| 1962 | 3,170 | 2,126 | 4,701 | 12,911 | 690 |
| 1963 | 3,316 | 2,181 | 5,144 | 15,158 | 697 |
| 1964 | 3,451 | 2,235 | 5,219 | 15,118 | 726 |
| 1965 | 4.143 | 2,305 | 5,697 | 14,885 | 808 |
| 1966 | 4,289 | 2,690 | 5,812 | 16,787 | 837 |

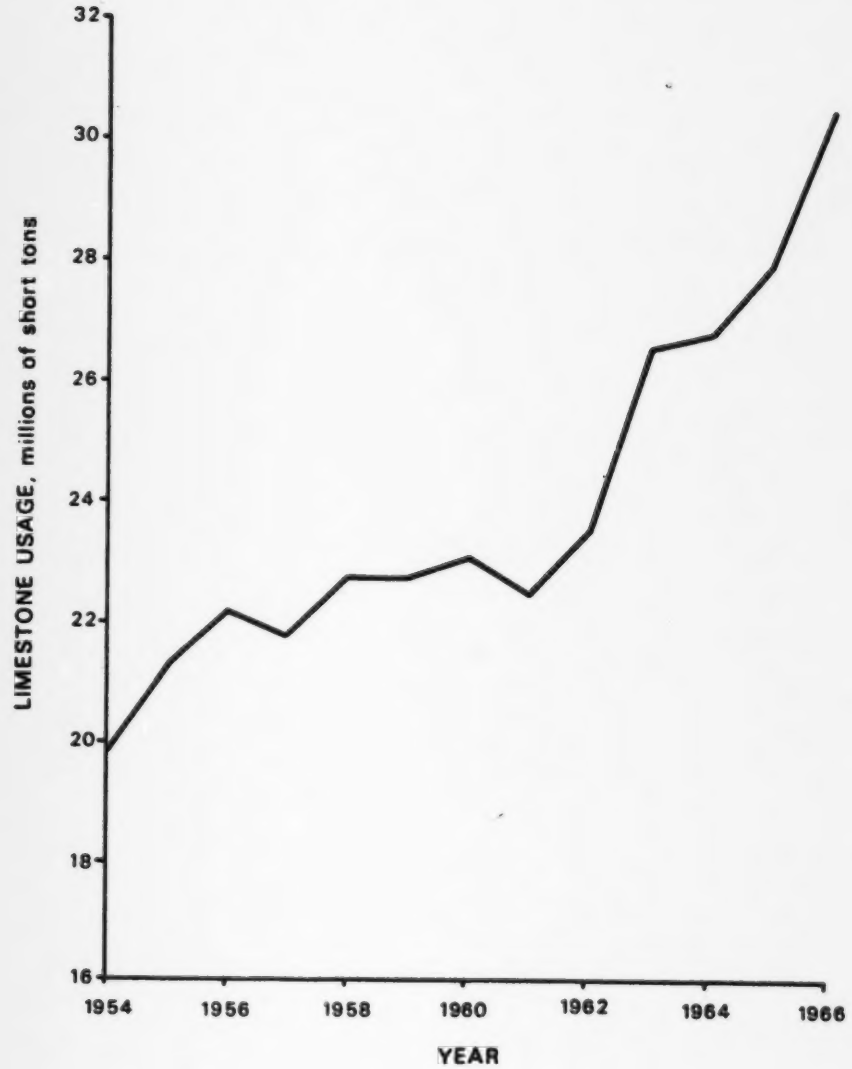



Figure 5. Agricultural Limestone Usage in the United States (Ref. 8)

from liming. Without lime the potential return from fertilizer applications can be reduced to 50 percent. It has been said that with good education and well-planned advertising, it is possible to increase the liming consumption sharply. It has also been predicted that in the next few years liming will increase by 15 to 20 percent with the release of more land from the soil bank for active cropping.

In addition to the complicated usage picture of aglime and rock, the value of sludge for this agricultural purpose will depend to a great extent upon its composition and the availability of the $P_2O_5$ content.

Table 9

NATIONAL AGRICULTURAL LIMESTONE CONSUMED (Ref. 8)

(80 million tons needed annually)

| Year | Tonnage | % of Needs |
|---|---|---|
| 1929 | 3,907,000 | 4.86 |
| 1936 | 6,565,587 | 8.16 |
| 1947 | 30,282,902 | 37.64 |
| 1954 | 18,974,945 | 23.52 |
| 1958 | 23,214,864 | 29.02 |
| 1963 | 26,118,856 | 32.68 |
| 1966 | 30,461,468 | 38.04 |

"SWEET MANURE"

It seemed that phosphate sludge could be used in agriculture as a phosphate lime or "sweet manure" by mixing it with compost or stabilized sewage sludge. Thus, the lime content would be beneficial in reducing soil acidity while organics and trace elements would derive from the compost or sewage sludge portion. Consequently, the market was reviewed for agricultural products from compost and sewage sludge.

Chemical composition of compost varies widely because of the quantity and composition of the constituent materials. On a dry basis it contains about 2% nitrogen, 2% phosphoric oxide, and 1% potash ($K_2O$). Compost and activated sewage sludge thus contain very little plant nutrient and trace element value, and their principal value is therefore as humus for soil building or conditioning. They are mainly

used by home gardeners and lawn keepers in certain areas and are incorporated with subsoil in the establishment of turf. Table 10 shows the amounts of compost and activated sludges consumed in the United States during 1964-65. Only 54,855 tons of compost and 88,340 tons of activated sewage sludge were consumed in the United States compared to 31,326,159 tons of total fertilizer consumption in that period.

During the middle fifties a number of composting plants were built in the United States. Most plants built relied on the sale of compost and salvaged materials for their primary income, coupled with a nominal payment by the municipality for disposal. Inability to dispose of large quantities of compost at a favorable price was a major factor in the closing of six U.S. composting plants during 1962-64. Recent discussion with officials of the Metropolitan Waste Conversion Corporation indicates that they are also having some problems in marketing the compost produced in their Houston plant.

Table 10

COMPOST AND ACTIVATED SEWAGE SLUDGE CONSUMED, BY REGION. YEAR ENDED JUNE 30, 1965 (Ref. 9)

| | Compost (Tons) | Activated Sewage Sludge (Tons) |
|---|---|---|
| New England | 1,371 | 6,641 |
| Middle Atlantic | 1,701 | 15,773 |
| South Atlantic | 4,971 | 16,090 |
| East North Central | 9,936 | 23,772 |
| West North Central | 673 | 7,050 |
| East South Central | 678 | 1,581 |
| West South Central | 528 | 4,992 |
| Mountain | 9,300 | 2,567 |
| Pacific | 25,597 | 9,805 |
| Alaska, Hawaii, and Puerto Rico | 100 | 69 |
| United States | 54,855 | 88,340 |

In some specific locations desirable arrangements might be developed for "sweet manure" although there is no widespread demand for such fertilizer in commercial agriculture now and no significant increase in demand is anticipated. Further, the larger the size of the plant the greater the difficulty expected in selling or disposing of the entire output in a given marketing area. Foreseeable economic conditions do not justify an estimate of the major portion of fertilizers or soil conditioners of "sweet manure" quality entering the market.

In view of this outlook, we recommended that the "sweet manure" studies originally proposed be deleted from the program. The primary consideration in applying lime-phosphate sludge to the soil, either directly or as a sweet manure, is the free lime content. Where soil sweetening is practiced, the rate of application, based either on free lime or limestone, is a reasonably well known art and "sweet manure" would be applied on the same basis. The humus building value of the sludges in the sweet manure mixture and the phosphate value per unit of "sweet manure" (though low) are desirable effects associated with the primary sweetening effect due to the lime (or calcium carbonate) content but do not add enough value to this product to make it economically attractive.

## SECTION V

## BENEFICIATION OF PHOSPHATE SLUDGE

From the market review of the potential of utilizing phosphate sludge the indication is that this material is hardly usable without preliminary beneficiation to increase its $P_2O_5$ content.

Natural phosphate deposits contain fluorapatite as the principal phosphate mineral, mixed with varying amounts of clay, quartz, and limestone as the predominent associated impurities. Hydraulic beneficiation is employed, and flotation is being used extensively in Florida.

It must be recognized that the problem with phosphate sludge may be entirely different, since we are dealing with a manufactured product and the surface characteristics, particle size, densities, and other relevant properties will depend on the process.

### RELEVANT PHOSPHORUS CHEMISTRY

According to Van Wazer (Ref. 15) the form of calcium phosphate in precipitates from aqueous media with excess calcium hydroxide is $Ca_5(OH)(PO_4)_3$. This, however, is a nominal composition and does not reflect various degrees of hydration that are coexistent. Further, he shows the following relationships that can be expected on calcining of the phosphate sludge:

1. $2Ca_5(OH)(PO_4)_3 \rightarrow 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O$
2. $Ca_4P_2O_9 = Ca_3(PO_4)_2 \cdot CaO$
3. $3Ca_4P_2O_9 + H_2O \rightarrow 2Ca_5(OH)(PO_4)_3 + 2CaO$
4. Both $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ in varying proportions can be expected on calcining depending upon the mole ratio of $CaO/P_2O_5$ in the sludge and the calcining temperature

In the following sections, we began by assuming that the initial precipitate was $Ca_3(PO_4)_2$ and remained as such throughout subsequent treatment. Later we assumed that

the initial precipitate was hydroxyapatite, $Ca_5(OH)(PO_4)_3$, that this was converted to $Ca_2P_2O_7$ on calcining and back to hydroxyapatite on subsequent treatment with water.

After reference to Van Wazer, the complexity of phosphate and phosphorous chemistry and the equations above, convinced us that, at least for the purposes of this study, it would be satisfactory to assume the initial precipitate and final product would be hydroxyapatite. It makes little difference to the present study whether the phosphate is considered as tri-calcium phosphate or hydroxyapatite. Figure 6 permits one to move freely among the various forms for expression of phosphorus content.

## BENEFICIATION BY CARBONATION

One approach to enrichment of phosphate content consists of carbonating the sludge to convert calcium carbonate and magnesium hydroxide to the bicarbonates in solution from which the insoluble calcium phosphate is removed by filtration. The calcium value of the solution is recovered by a fractional precipitation with lime water, and if desired, the calcium value is recovered by ammoniation. This potential method of phosphate enrichment is illustrated in Figures 7 and 8, which also indicate methods of converting the phosphate to other products with recovery and recycle of available lime value. The desirability of such additional processing at the treatment plant site and process costs would have to be determined in order to decide whether such additional operations were justified.

In the laboratory, the feasibility of enriching the phosphate content of sludge through carbonation was explored. With chemical reagents the steps in phosphate removal by liming were simulated so as to obtain a sludge with the following approximate composition:

| | |
|---|---|
| $Ca_3(PO_4)_2$ | 50% |
| $CaCO_3$ | 20% |
| $Mg(OH)_2$ | 30% |

Carbon dioxide was sparged into an aqueous suspension of this material in two steps. The solid remaining from the second carbonation was filtered off, dried, and weighed,

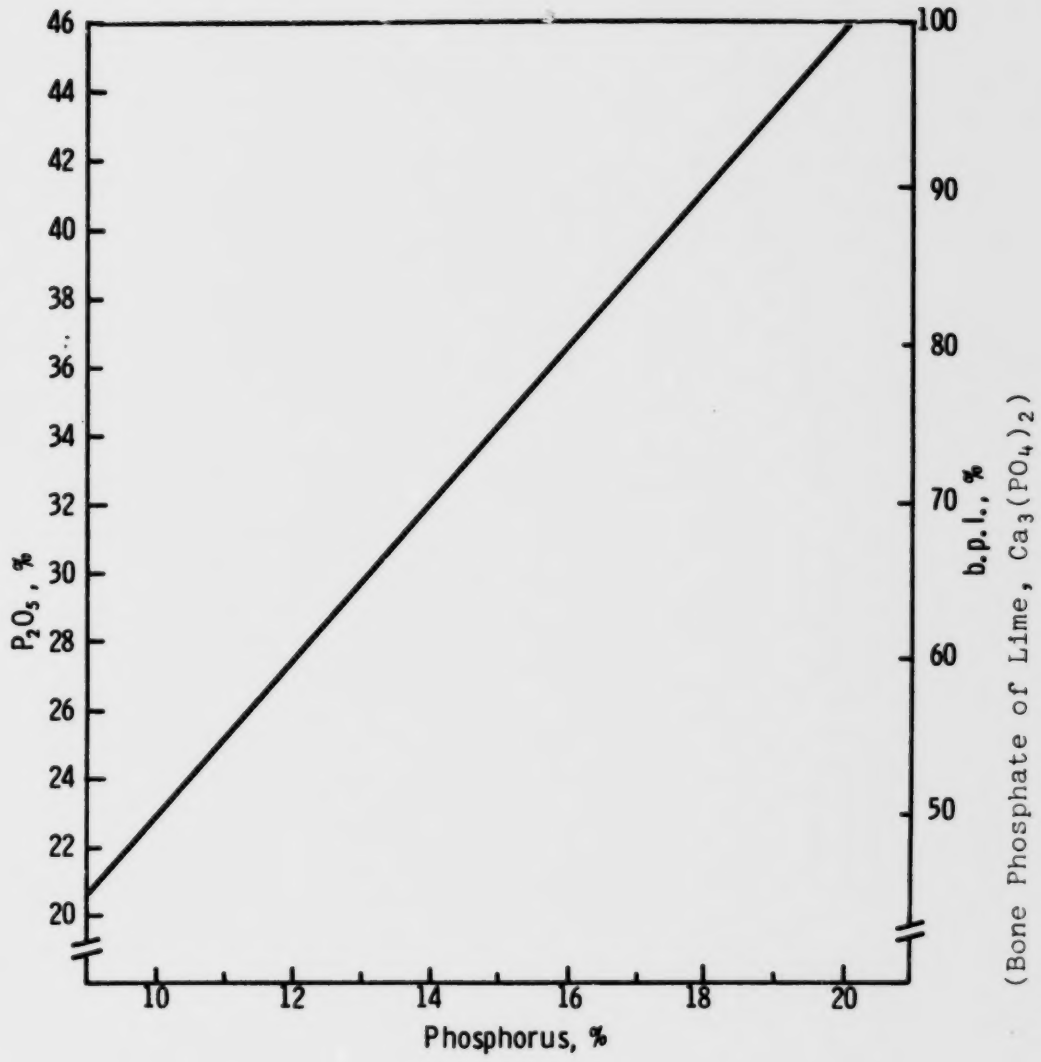



Figure 6. Relationship of Equivalent Expressions for Phosphorus Content

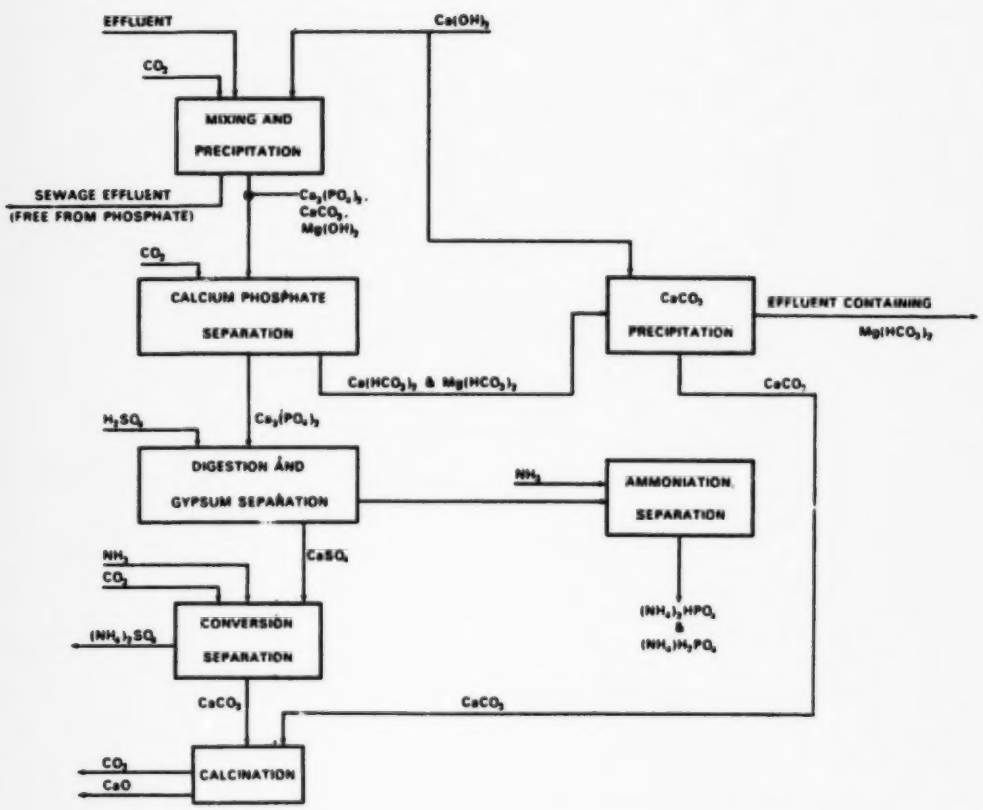



Figure 7. Calcium Phosphate Separation and Acidulation with Sulfuric Acid

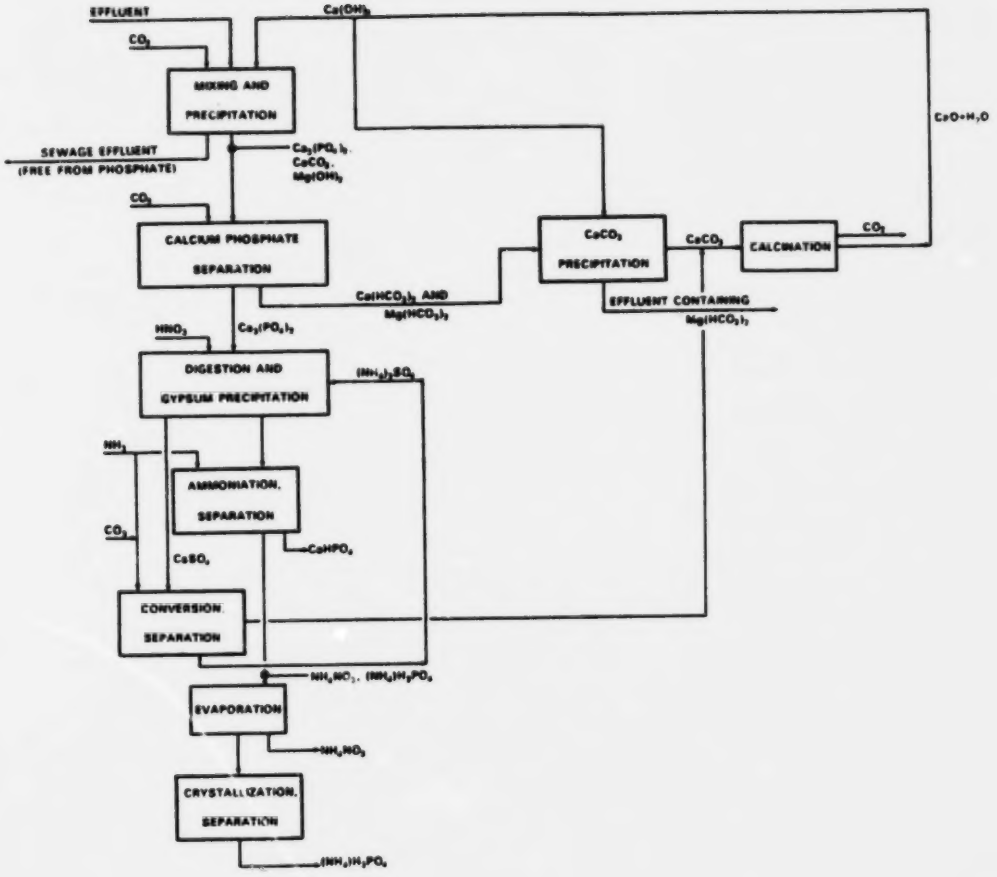



Figure 8. Calcium Phosphate Separation and Acidulation with Nitric Acid

yielding 4.47 grams of calcium phosphate, as identified by IR spectrum. The theoretical yield from the experiment was 4.96 grams. According to IR analysis, the other two components were not present in the final "rock." Thus, it appeared feasible that the carbonation technique could effect enrichment of the sludge phosphate content.

A relatively simple, continuous leaching process was visualized employing off-gas from the claciner at two steps. The bicarbonate solution would be heated to about 60°C by direct contact with kiln gas wherein the calcium and magnesium would precipitate as the carbonate and hydroxide, respectively. The cooled kiln gas would go to the leacher for bicarbonate formation. It is also theoretically possible, if desirable, to separate the calcium from the magnesium by careful adjustment of the pH of the bicarbonate solution in two stages. The efficiency and economics of these approaches would depend upon material balances around the system.

A schematic of the first part of a potential process on this basis for phosphate precipitation with lime and reuse of the lime is shown in Figure 9. Calculations were based on a dosage of 400 mg CaO per liter of effluent. One hundred percent calcium recovery and 100% phosphate removal from effluent were assumed. Effluent concentrations as phosphorus were taken as 5, 10, and 15 mg/l. The completion of a cycle represents the point after all the recovered sludge was calcined. As Figure 10 shows, a sludge with a high percentage $Ca_3(PO_4)_2$ can be recovered after only four recycles of treatment when effluent contains 15 mg/l as phosphorus. An effluent with 5 mg/l as phosphorus will yield a sludge of about 44% $Ca_3(PO_4)_2$ after 12 cycles. Yields for effluents with 10 and 15 mg/l as phosphorus are 62% and 72% [as $Ca_3(PO_4)_2$], respectively for 12 cycles.

Make-up CaO must be added to the sludge after each cycle to keep the CaO concentration at 400 mg/l of effluent. Make-up CaO values are shown in Table 11. Due to the precipitation of $Ca_3(PO_4)_2$ and the make-up lime, the weight of the sludge increases after each cycle. The number of possible cycles, therefore, will be limited by the capability of the process equipment. Figures for sludge buildup are shown in Table 12.

A schematic for the second part of the conceptual process, calcium phosphate enrichment of the sludge by removal of calcium as the bicarbonate, is shown in Figure 11. The sludge shown in Figure 9 as going to Phase II is assumed

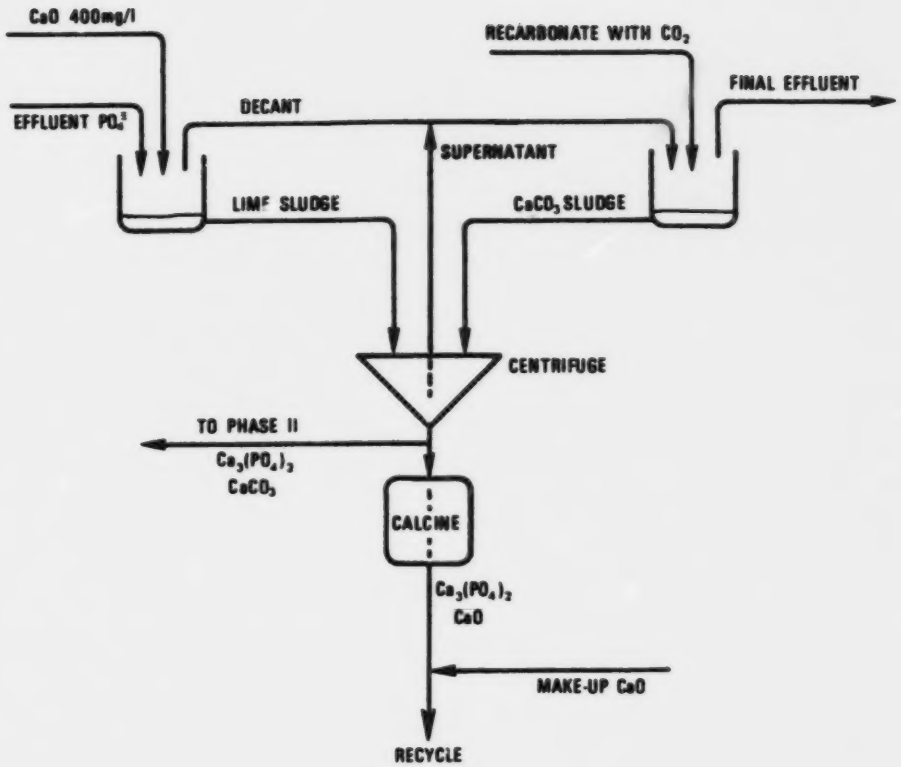



Figure 9. Schematic for Phosphate Precipitation with Lime and Lime Recovery

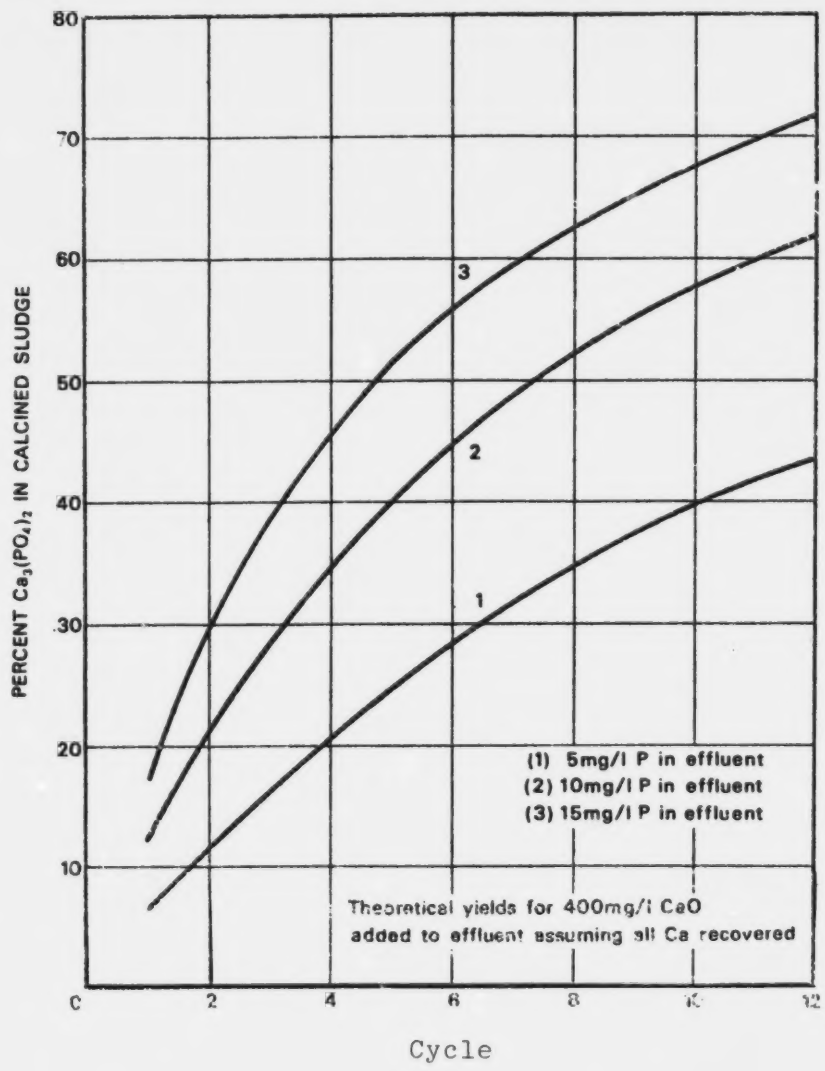



Figure 10. Calculated Effect of Number of Treatment Cycles on Percent $Ca_3(PO_4)_2$ in Calcined Sludge

Table 11

MAKE-UP CaO FOR RECYCLE (mg/l EFFLUENT)*

| | |
|---|---|
| 5 mg/l P in effluent | 13.5 |
| 10 mg/l P in effluent | 27.0 |
| 15 mg/l P in effluent | 40.5 |

*Theoretical yields for 400 mg/l CaO added to effluent assuming all Ca recovered.

Table 12

WEIGHT OF CALCINED SLUDGE AFTER CYCLE (mg/l EFFLUENT)*

| | Phosphorous in Effluent | | |
|---|---|---|---|
| Cycle | 5 mg/l | 10 mg/l | 15 mg/l |
| 1 | 411.5 | 423 | 434.5 |
| 2 | 436.5 | 473 | 509.5 |
| 3 | 461.5 | 523 | 584.5 |
| 4 | 486.5 | 573 | 659.5 |
| 5 | 511.5 | 623 | 734.5 |
| 6 | 536.5 | 673 | 809.5 |
| 7 | 561.5 | 723 | 884.5 |
| 8 | 586.5 | 773 | 959.5 |
| 9 | 611.5 | 823 | 1034.5 |
| 10 | 636.5 | 873 | 1109.5 |
| 11 | 661.5 | 923 | 1184.5 |
| 12 | 686.5 | 973 | 1259.5 |

*Theoretical yields for 400 mg/l CaO added to effluent assuming all Ca recovered.

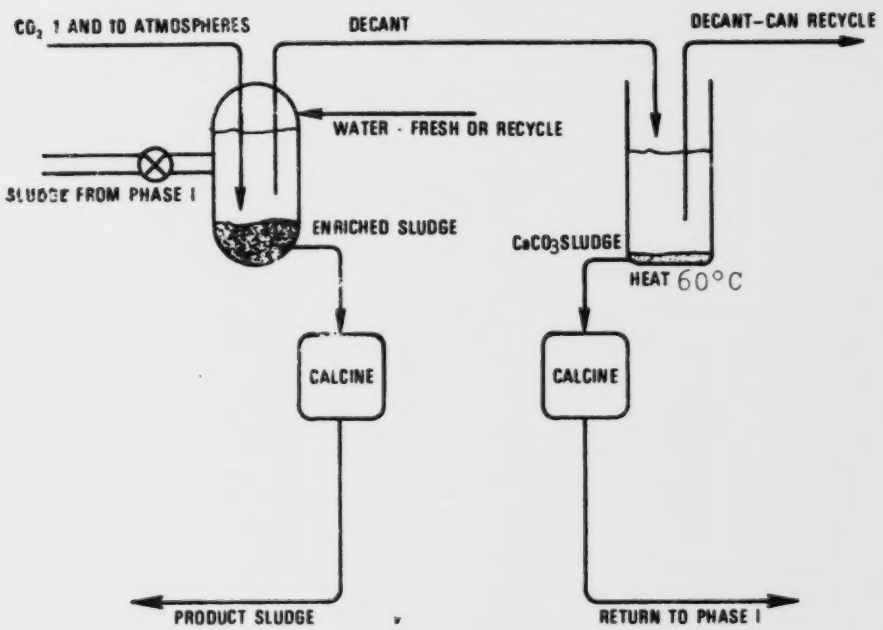



Figure 11. Schematic for Calcium Phosphate Enrichment of Sludge by Carbonation

to consist of calcium phosphate and calcium carbonate. The insoluble carbonate dissolves when converted to the bicarbonate. The solubility of $CaCO_3$ is 0.819 g/l of water and 2.05 g/l of water under 1 and 10 atmospheres partial pressure of $CO_2$, respectively (Ref. 12). The water in which the $CaCO_3$ is dissolved is decanted from the sludge and heated to 60°C, causing precipitation of the carbonate. The calcium carbonate can be calcined and reused in the liming of fresh feed to the process. The water can be recycled.

Figure 12 shows the liters of water per 100 grams sludge needed to raise the percent $Ca_3(PO_4)_2$ in the sludge, at 1 and 10 atmospheres partial pressure $CO_2$. At 10 atmospheres, the amount of water needed to reach any specified concentration of phosphate in the sludge is approximately 40% the amount of water needed at 1 atmosphere. Converted to gallons and tons, these data are shown in Table 13 with $Ca_3(PO_4)_2$ in the final product at 65%.

Table 13

GALLONS OF WATER NEEDED TO RAISE PERCENT $Ca_3(PO_4)_2$ IN SLUDGE TO 65% AT 1 AND 10 ATMOSPHERES PARTIAL PRESSURE OF $CO_2$

| % $Ca_3(PO_4)_2$ in Sludge* | | Gallons of Water per Ton Product | Gallons per Minute for 1 Ton/Day Yield | Partial Pressure $CO_2$ Atmospheres |
|---|---|---|---|---|
| From | To | | | |
| 10 | 65 | 2,720,000 | 1,889 | 1 |
| 20 | 65 | 1,079,400 | 750 | 1 |
| 30 | 65 | 548,300 | 381 | 1 |
| 40 | 65 | 299,000 | 208 | 1 |
| 50 | 65 | 143,000 | 99 | 1 |
| 10 | 65 | 930,500 | 646 | 10 |
| 20 | 65 | 428,500 | 298 | 10 |
| 30 | 65 | 224,300 | 156 | 10 |
| 40 | 65 | 122,000 | 85 | 10 |
| 50 | 65 | 64,000 | 45 | 10 |

*Assume sludge consists entirely of calcium phosphate and lime.

The carbonation method was performed on sewage sludge samples from the Lake Tahoe plant. The carbonation and separation in the laboratory was accomplished by passing carbonated water through a column packed with 30 grams of phosphate sludge from the Lake Tahoe Project with the phosphorus and calcium content shown in Table 14.

Table 14

EFFECT OF CARBONATION ON PHOSPHATE CONTENT OF CALCINED SLUDGE

| | Initially | After Enrichment |
|---|---|---|
| Phosphorus as $PO_4$ | 22.4% | 26% |
| Calcium as Ca | 32.2% | 28.4% |
| Mixed organics, Mg, etc. | 45.4% | -- |

Since the pH of bicarbonate solutions is above 7.0 the flow rate through the column was regulated to keep the pH of the effluent water at about pH of 7.0. One liter of carbonated water (pH 4.5) was passed through the column, heated to precipitate the $CaCO_3$, filtered to separate the $CaCO_3$, and recarbonated for reuse in the column. Fourteen one-liter cycles were run through the column. The precipitates from the third and eighth cycles showed no phosphate by the Hack Orthophosphate Test. The phosphate content of the sludge in the column was increased to 26% after 14 one-liter cycles, as shown in the analysis results in Table 14. From Figure 12 a phosphate content of about 25-26% is predicted after 14 liters of water addition.

From these results, then, the calculations show that with 10 mg/l of phosphorus in the feed, the sludge mass increases by 25% after three cycles, at which point the concentration of $Ca_3(PO_4)_2$ in the sludge is about 30%. To remove calcium and magnesium as bicarbonates and leave the insoluble calcium phosphate requires a water usage rate of about 350 gpm per daily ton of calcium phosphate produced. Furthermore, the calcium bicarbonate has to be reprecipitated for recovery. Consequently, this approach appears less than marginal and suggests a search for other means of phosphate enrichment.

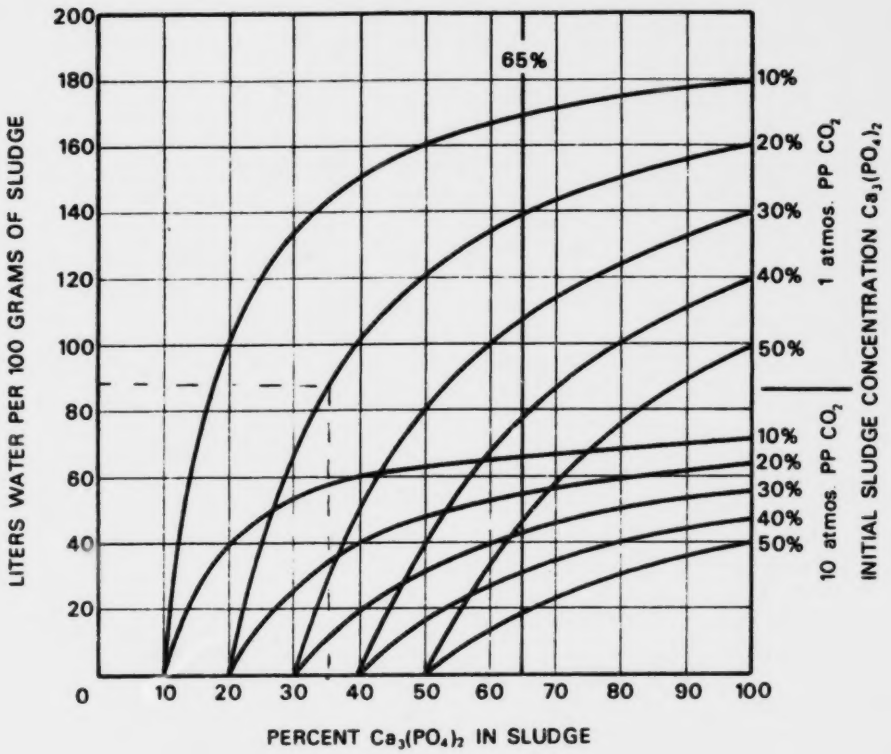



Figure 12. Calculated Water Requirement to Increase Percent $Ca_3(PO_4)_2$ in the Sludge at 1 and 10 Atmospheres Partial Pressure of $CO_2$ (Sludge is Assumed to Consist Only of CaO and $Ca_3(PO_4)_2$).

Example: Starting with 100 grams of sludge with initial 20% calcium phosphate concentration and partial pressure of $CO_2$ at 1 atmosphere, 90 liters of water would be required to raise the $Ca_3(PO_4)_2$ concentration to 34% by dissolving away $CaCO_3$; 140 liters would be required to raise the $Ca_3(PO_4)_2$ concentration to 65%.

## THERMOCHEMICAL SEPARATION

Owing to the similar densities and flotational characteristics of apatite and calcite, an approach to beneficiation described by the Irkutsk State Scientific Research Institute of Rare Metals (Irgiredmet) and later by the Mining Metallurgical Institute in Kilsk (Refs. 13, 14) was considered.

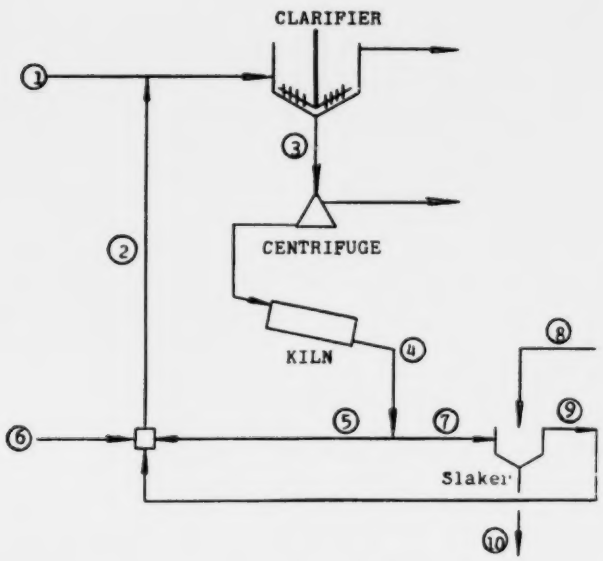
With natural rock, this treatment is based on the thermal decomposition of carbonates at 900-1000°C with subsequent separation of calcium and magnesium oxides in the form of a suspension of very fine particles. The coarse apatite, or $Ca_3(PO_4)_2$, remains unchanged and settles to the bottom, while the fines are floated off, or classified, with water.

When the treatment was applied to "synthetic" rock, there was no evidence of phosphate enrichment in the sediment. Floated and settled fractions had the same phosphate content. We believe this is explained by the uniformity of particle size of the precipitated salts.

Repeated attempts to thermally beneficiate the phosphate content of study samples or synthesized sludge were unsuccessful. The apparent explanation for the difference in results obtained with natural and "synthetic" phosphate rock is attributed to the difference in structure of the two materials. In the natural rock, the calcite and apatite exist in some specific "particle" size which is, in effect, a localized concentration of the materials. On thermal treatment the calcite is decomposed, but the apatite is not and thus it basically retains its original "particle" size. In water, the lime from the calcite slakes and forms fine particles of $Ca(OH)_2$ which are easily floated, or classified, away from the larger apatite particles. In the "synthetic" phosphate rock, or sludges, the particle sizes formed are, throughout, about the same for both compounds so that there was always essentially no separation during classification.

## MODIFIED THERMAL BENEFICIATION

An alternative means of enriching the phosphate content of the sludge is a modification of the thermal treatment approach. Instead of floating off (or classifying) the lime particles, the method consists of dissolving out all the lime as $Ca(OH)_2$, from a side stream of calcined sludge. The concept is shown schematically in Figure 13. With 10 mg/liter of phosphorus in the feed, sludge mass




Key to Figure 13

1 - Secondary effluent to clarifier
2 - Lime slurry from mixer
3 - Lime sludge to centrifuge
4 - Calcined sludge from kiln
5 - Recycle calcined sludge to mixer
6 - Makeup lime to mixer
7 - Calcined sludge purge stream to dissolving tank
8 - Fresh water
9 - Calcium hydroxide solution to recycle
10 - Phosphate "rich" sludge from dissolving tank

Figure 13. Conceptual Schematic Flow Diagram of Process for Sludge Phosphate Enrichment by Modified Thermal Approach

increases by about 25% after three to four cycles at which time calcium phosphate content is about 30% and a side-stream (7) is taken off at a rate to maintain the phosphate content of the main sludge stream essentially constant. The amount of side stream bleed-off chosen here is arbitrary to allow a maximum of 25% increase in sludge mass. The side stream is slaked with fresh water, thus removing the caustic and leaving hydroxy-apatite. The caustic effluent is used to slurry and slake the recycle calcine and fresh lime make-up. Assuming calcium hydroxide solubility to be 1.5 g/liter, fresh water usage would amount to about 260 gpm per daily ton of phosphate product.

This alternative means of enriching the sludge phosphate content appears more attractive than the carbonation method. It is less complex and more economical in water usage. General material balances for the ideal case are shown in Table 15 with assumptions employed. The fifth cycle is typical of steady state operation after the side stream process is started, again, assuming 25% allowable sludge buildup.

Subsequently, a detailed material balance was made for this process based on a typical wastewater feed composition. Feed analysis is shown in Table 16 along with the calculated analyses of the effluent streams from the overall phosphate removal operation which is shown schematically in Figure 14. The process material balance representing steady state operation per million gallons of feed is shown in Table 17.

It is interesting to note in this particular case that there is a net gain in calcium, because of the high level of calcium in the feed. For such condition the process would be more than self-sustaining on a lime basis and thus potentially could produce lime as a by-product, as well as hydroxyapatite, in areas where the water contains high calcium levels. Recovery of this material, as calcium carbonate, is indicated through the addition of a second carbonation step and clarifier.

Assuming calcium hydroxide solubility of 1.0 g/l, fresh water usage, stream 8, per daily ton of hydroxyapatite, is about 480 gpm. However, only about half of this is wasted in recycling lime back to the phosphate precipitation step: streams 9, 13, 2. The remaining half leaves in stream 17, whose apparent quality suggests its recycling to stream 8. In this manner, fresh water make-up requirement is reduced to about half, or about 240 gpm per daily ton of phosphate product. With feed phosphate

Table 15

MATERIAL BALANCE--IDEAL CASE PHOSPHATE SLUDGE BENEFICIATION

| Stream No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | FIRST CYCLE | | | | | |
| Phosphorus, P, lb. | 83 | - | - | - | - | - | - | - | - | - |
| Lime, CaO, lb. | - | 3340 | - | 3190 | 3190 | - | - | - | - | - |
| Ca $CO_3$ lb. | - | - | 5514 | - | - | - | - | - | - | - |
| $Ca_5(OH)(PO_4)_3$ lb. | - | - | 450 | - | - | - | - | - | - | - |
| $Ca_2 P_2 O_7$ lb. | - | - | - | 343 | 343 | - | - | - | - | - |
| Water, gal. | $1x10^6$ | - | - | - | - | - | - | - | - | - |
| | | | | | FIFTH CYCLE | | | | | |
| phos., P. lb. | 83 | - | - | - | - | - | - | - | - | 83 |
| Lime, CaO, lb. | - | 3340 | - | 3190 | 2393 | 250 | 797 | - | 697 | - |
| Ca $CO_3$ lb. | - | - | 5514 | - | - | - | - | - | - | - |
| $Ca_5(OH)(PO_4)_3$ lb. | - | 1350 | 1800 | - | - | - | - | - | - | 450 |
| $Ca_2 P_2 O_7$, lb. | - | - | - | 1374 | 1030 | - | 344 | - | - | - |
| Water, gal. | $1x10^6$ | $8.4x10^4$ | - | - | - | - | - | $8.4x10^4$ | $8.4x10^4$ | - |

Assumptions:

a. $1x10^6$ gal feed
b. 10 mg/ℓ Phosphorous in feed
c. 400 mg/ℓ CaO dosage
d. 100% Phosphorous removal
e. all solids are lime products and phosphate
f. solubility of $Ca(OH)_2$ is 1.5 g/ℓ at conditions
g. lime sludge is calcined and recycled x times
h. fresh lime added to make up for phosphate precipitated
i. phosphorous precipitated as hydroxyapatite $[Ca_5(OH)(PO_4)_3]$
j. mg/ℓ = ppm
k. no solids in clarifier or centrifuge effluents

Table 16

FEED AND EFFLUENT COMPOSITION

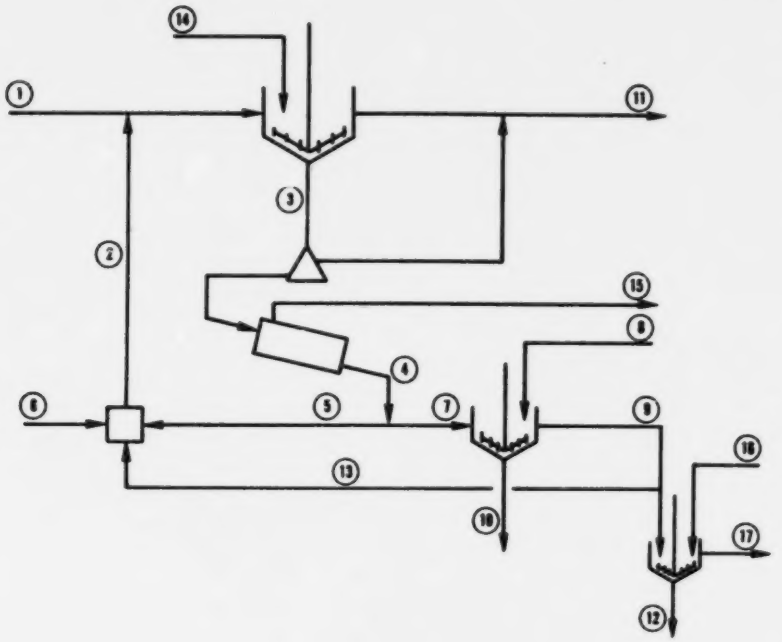
| Stream | ① mg/l | ⑪ mg/l | ⑰ mg/l |
|---|---|---|---|
| COD | 60 | --- | |
| Susp. Solids | 30 | --- | |
| Dissolved Solids | 750 | 546.8 | |
| Ammonia (as N) | 20 | 18.7 | |
| Sodium | 110 | 102.8 | |
| Potassium | 12 | 11.2 | |
| Calcium | 60 | 3.5 | 3.7 |
| Magnesium | 20 | 3.9 | 2.6 |
| Chloride | 80 | 74.8 | --- |
| Sulfate | 50 | 46.7 | --- |
| Phosphate (as P) | 10 | 0.93 | --- |
| Bicarbonate ($HCO_3$) | 200 | 100.1 | --- |
| $Ca(HCO_3)_2$ | --- | --- | 9.5 |
| $Ca_5(OH)(PO_4)_3$ | --- | --- | --- |
| MgO | --- | --- | 4.2 |

## Table 17

## THEORETICAL MATERIAL BALANCE AROUND PHOSPHATE REMOVAL AND RECOVERY PROCESS

| Stream | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Suspended Solids, lb. | 250 | 5229 | 10141 | 6974 | 5230 | ---- | 1744 | ---- | ---- | 871 | ---- |
| Dissolved Solids, lb. | 6260 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 4883 |
| Ammonia, N, lb. | 167 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 167 |
| Sodium, lb. | 918 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 918 |
| Potassium, lb. | 100 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 100 |
| Calcium, lb. | 502 | 2679 | 3149 | 3149 | 2362 | ---- | 787 | ---- | 625 | 162 | 32 |
| Magnesium, lb. | 167 | 398 | 530 | 530 | 398 | ---- | 132 | ---- | 3 | 129 | 35 |
| Chloride, lb. | 668 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 668 |
| Sulfate, lb. | 417 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 417 |
| Bicarbonate, lb. | 1669 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 894 |
| Phosphorus, P, lb. | 83.5 | 225 | 300 | 300 | 225 | ---- | 75 | ---- | ---- | 75 | 8.5 |
| Lime, CaO, lb. | ---- | 3340 | ---- | 3862 | 2896 | ---- | 966 | ---- | 874 | ---- | ---- |
| $CaCO_3$, lb. | ---- | ---- | 6244 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| $Ca_2P_2O_7$, lb. | ---- | 924 | ---- | 1232 | 924 | ---- | 308 | ---- | ---- | ---- | ---- |
| $Ca_5(OH)(PO_4)_3$, lb. | ---- | ---- | 1624 | ---- | ---- | ---- | ---- | ---- | ---- | 406 | ---- |
| MgO, lb. | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 218 | ---- |
| $CO_2$, lb. | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Water, gal. | $1x10^6$ | $0.7x10^5$ | ---- | ---- | ---- | ---- | ---- | $1.4x10^5$ | $1.4x10^5$ | ---- | $1.07x10^6$ |

| Stream | 12 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|
| Suspended Solids, lb. | 1238 | ---- | ---- | ---- | ---- | ---- |
| Dissolved Solids, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| Ammonia, N, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| Sodium, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| Potassium, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| Calcium, lb. | 306 | 317 | ---- | ---- | ---- | 2.1 |
| Magnesium, lb. | 0.01 | 1.5 | ---- | ---- | ---- | 1.5 |
| Chloride, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| Sulfate, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| Bicarbonate, lb. | ---- | ---- | ---- | ---- | ---- | --- |
| Phosphorus, P, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| Lime, CaO, lb. | ---- | 444 | ---- | ---- | ---- | ---- |
| $CaCO_3$, lb. | 764 | ---- | ---- | ---- | ---- | 5.4 |
| $Ca_2P_2O_7$, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| $Ca_5(OH)(PO_4)_3$, lb. | ---- | ---- | ---- | ---- | ---- | ---- |
| MgO, lb. | 0.7 | ---- | ---- | ---- | ---- | 2.8 |
| $CO_2$, lb. | ---- | ---- | 3260 | 2746 | 406 | ---- |
| Water, gal. | ---- | $0.7x10^5$ | ---- | ---- | ---- | $0.7x10^5$ |




Key to Figure 14

1 - Secondary effluent to clarifier
2 - Lime slurry from mixer
3 - Lime sludge to centrifuge
4 - Calcined sludge from kiln
5 - Recycle calcined sludge to mixer
6 - Make-up lime to mixer
7 - Calcined sludge purge stream to dissolving tank
8 - Fresh water or stream No. 17 recycle
9 - Calcium hydroxide solution to recycle (13) and carbonation (16) for lime recovery
10 - Phosphate "rich" sludge from dissolving tank
11 - Tertiary effluent to further treatment or discharge
12 - Calcium carbonate sludge to centrifuge and kiln
14 - Carbon dioxide for pH control and excess lime recovery
15 - Kiln off-gas possible to (14) and/or (16)
16 - Carbon dioxide for pH adjustment and lime recovery
17 - Discharge to receiving water

Figure 14. Schematic Flow Diagram for Phosphate Enrichment of Lime Sludge

content at 10 mg/l, as phosphorus, a 5-million gpd treatment plant would produce roughly one ton per day of phosphate product.

To test the feasibility of this paper process, calcined sludges were synthesized from CaO and $Ca_2P_2O_7$ with the latter constituent in the range of 5-30%. Samples of the calcined sludge were slaked with one-liter portions of deionized water and filtered. The $Ca_2P_2O_7$ content of the residues was determined. The filtrates from the operation above were carbonated, filtered, and tested for Ca. The effect of one-cycle slaking on $Ca_2P_2O_7$ content in the sludge is shown in Table 18 below:

Table 18

EFFECT OF SLAKING ON PHOSPHATE CONTENT OF CALCINED SYNTHETIC SLUDGE

| Sludge $Ca_2P_2O_7$ Content | |
|---|---|
| Initial, % | Final, % |
| 5 | 7.0 |
| 10 | 14.1 |
| 15 | 21.1 |
| 20 | 28.1 |
| 25 | 35.0 |
| 30 | 42.2 |

The percent increase in phosphate content is constant at about 40%, indicating $Ca(OH)_2$ solubility for these conditions of 1.9 g/l.

Recovery of Ca from the effluents by carbonation ranged from 50-75% efficient. The relatively low efficiency is attributed to poor control of carbonation in this particular series of studies. Equilibrium in the $CaO-H_2O-CO_2$ system is not instantaneous so that the desired pH of 9-9.5 was frequently overshot on the low side and some Ca dissolved as bicarbonate.

## TREATMENT OF SECONDARY EFFLUENT AND SLUDGE ENRICHMENT

The entire procedure was tested with sewage effluent. Secondary (trickling filter) effluent from the Dayton Sewage Plant was treated with lime to remove phosphates. Twice, the entire treatment and sludge beneficiation process was carried through four cycles, each cycle representing treatment of one liter of effluent.

The initial lime dose of 400 mg raised pH above 11. Make-up lime thereafter averaged 50 mg per cycle. Calcining was effected in a muffle furnace at 1800°F for 1-1/2 hours. All of the calcined sludge was recycled, together with fresh lime make-up, into each fresh liter of effluent. All effluents from the system were analyzed for total hardness, Ca hardness and ortho-phosphate content. Phosphate content was determined in the final sludge.

Effluent quality results for the phosphate removal step are shown in Table 19 (refer to Figure 14 for stream numbers).

Table 19

EFFLUENT QUALITY FROM LABORATORY TREATMENT OF SECONDARY EFFLUENT FOR PHOSPHATE REMOVAL

| Cycle (1 liter ea.) | Feed,* mg/l | | | Effluent,* mg/l | | | Effluent pH |
|---|---|---|---|---|---|---|---|
| | Ca | Mg | $PO_4$ | Ca | Mg | $PO_4$ | |
| 1 | 78 | 13 | 18.4 | 77 | 6 | 1.75 | 8.7 |
| 2 | 78 | 13 | 18.4 | 81 | 18 | 2.88 | 8.0 |
| 3 | 78 | 13 | 18.4 | 43 | 17 | <1.0 | 9.0 |
| 4 | 78 | 13 | 18.4 | 23 | 6 | <1.0 | 9.2 |
| 1 | 93 | 4 | 16.5 | 56 | 3 | <1.0 | 8.9 |
| 2 | 93 | 4 | 16.5 | 71 | 1 | <1.0 | 8.5 |
| 3 | 93 | 4 | 16.5 | 33 | 3 | <1.0 | 9.2 |
| 4 | 93 | 4 | 16.5 | 27 | 1 | <1.0 | 9.0 |

*Feed, stream - 1
Effluent, stream - 11

From effluent analysis, the phosphate content of sludge (stream 4) from series 1 was calculated to lie in the range 65.4-67.4 mg as $PO_4$. Sludge analysis revealed the $PO_4$ content to be 65.3 mg.

Again, pH data indicate poor control during carbonation following phosphate removal. However, it is interesting to note that, when control is satisfactory, as in cycles 3 and 4 each series, it does appear that a net gain in Ca will occur. Thus, in areas of Ca hardness, this phosphate removal process should at least be self-sustaining on lime basis, and may even generate product lime.

To enrich the calcined sludge from cycle 4 in each series, the slaking was performed with Dayton tap water, with calcium hardness of about 46 mg/l. In this instance, solubility of $Ca(OH)_2$ was 1.6 g/l.

Results of the sludge enrichment steps for each series were as follows:

| Series | Feed P, ppm | % $Ca_3(PO_4)_2$, Calcined Sludge Before Slaking | After Slaking |
|---|---|---|---|
| 1 | 6 | 15.6 | 24.7 |
| 2 | 5 | 11.8 | 19.4 |

In the earlier ideal calculations, it was noted that with 10 ppm P in the feed, the sludge mass would increase to 1.25 times the initial sludge mass in about 4 cycles, at which point calcium phosphate concentration in the sludge would be in the range of 25-30%. With real secondary effluent, with about half as much phosphorus, the calcium phosphate content of the calcined sludge, before slaking, after 4 cycles is, as indicated in the table above, roughly half as much (see Table 15, Stream 4, fifth cycle).

## MATHEMATICAL MODEL

It is obvious that process operation depends to a major extent on feed composition. In order to evaluate the process under a wide variety of feed conditions, a set of equations was developed incorporating all known variables to permit simulation of the process operation. This simple mathematical model of the system for phosphate removal represents the entire system shown in Figure 14.

The model is designed for steady state operation per million gallons of feed to the system at a constant lime dosage of 400 mg/l. It produces two significant outputs:

(1) sludge buildup at specified recycle, and (2) concentrations in effluent streams at steady state. Precipitated phosphorus is assumed to exist as $Ca_5OH(PO_4)_3$ in all streams and suspended solids are assumed to be 75% volatile. The program can be modified to eliminate this second assumption and insert it as data input.

To be consistent, we illustrate the model for the case where feed composition is as shown in Table 16, Stream 1. Values of input variables are shown in the top section of Table 20. The center section of Table 20 shows the rate of sludge buildup over the original quantity on total recycle. By original sludge is understood that which is obtained from the addition of 400 ppm lime to fresh secondary effluent. As this sludge is recycled it increases in mass. The lower section of Table 20 gives results for steady state operation with the sludge buildup limited to 1.25 times the "original sludge." Weight and concentration of significant constituents in product streams from the phosphate enrichment portion of the system are presented. These results can be compared with those in Table 17.

Several points invite comment or clarification. In the present model, "analytical" values of effluent composition, as well as composition of the feed stream, are used as input to the program. First, it would be more desirable if the model will predict the compositions of all streams in the system when analytical values for the feed stream are introduced. This would broaden usefulness of the model. A requirement for this is knowledge of the values of "removal factors" and their relationship to lime dosage. For example, we might say that, at 400 mg/l lime dosage, 0.95 of the entering phosphorus is removed, 0.90 of the entering Mg is removed, 0.93 of the entering carbonate is removed. At lower lime dosages, presumably, these factors would be smaller. It may be possible, for modeling purposes, to derive these factors statistically from existing data at the three WQO pilot installations employing liming for phosphate removal.

The equations of the model employ a handbook value for $Ca(OH)_2$ solubility which is adjusted by considering hardness of fresh water used in the lime slaking step. This particular point of slaked lime solubility requires, for better precision of the model, the same type of definition discussed above.

The "attrition factor" is simply a loss factor, values of which are arbitrarily assumed in lieu of relevant data.

## Table 20

## MATHEMATICAL MODEL PROGRAM PRINTOUT

INPUT VARIABLES

| | |
|---|---|
| CA CONTENT OF STREAM I (MG/L) AS CA | 60.00 |
| CA CONTENT OF STREAM II (MG/L) AS CA | 3.50 |
| MG CONTENT OF STREAM I (MG/L) AS MG | 20.00 |
| MG CONTENT OF STREAM II (MG/L) AS MG | 3.90 |
| P CONTENT OF STREAM I (MG/L) AS P | 10.00 |
| P CONTENT OF STREAM II (MG/L) AS P | 1.00 |
| SUSPENDED SOLIDS CONTENT OF STREAM I (MG/L) | 30.00 |
| ATTRITION FACTOR | 1.00 |
| BICARBONATE CONTENT OF STREAM I AS HCO3= (MG/L) | 200.00 |
| HARDNESS OF FRESH WATER AS CACO3 (MG/L) | 0.00 |
| SLUDGE BUILD-UP ALLOWED (0-1) | 0.25 |

STEADY STATE FOR 1 MILLION GALLONS WITH 400 MG/L LIME DOSE IN STREAM 1
ASSUMING A. ALL P AS CA5OH(PO4)3 IN STREAM 10
B. 75 PER CENT SUSPENDED SOLIDS VOLATILE

KX= WEIGHT IN LBS OF STREAM 4 AFTER X CYCLES WITH TOTAL RECYCLE
LX= PER CENT SLUDGE WEIGHT BUILD-UP IN STREAM 4 AFTER X CYCLES WITH TOTAL RECYCLE

| | | | LBS. | | PER CENT |
|---|---|---|---|---|---|
| CYCLE NUMBER | 1 | KX | 4455.52 | LX | 0.00 |
| CYCLE NUMBER | 2 | KX | 5573.04 | LX | 25.08 |
| CYCLE NUMBER | 3 | KX | 6690.57 | LX | 50.16 |
| CYCLE NUMBER | 4 | KX | 7808.09 | LX | 75.24 |
| CYCLE NUMBER | 5 | KX | 8925.61 | LX | 100.32 |
| CYCLE NUMBER | 6 | KX | 10043.14 | LX | 125.40 |
| CYCLE NUMBER | 7 | KX | 11160.66 | LX | 150.49 |
| CYCLE NUMBER | 8 | KX | 12278.18 | LX | 175.57 |
| CYCLE NUMBER | 9 | KX | 13395.71 | LX | 200.65 |
| CYCLE NUMBER | 10 | KX | 14513.23 | LX | 225.73 |

OUTPUT

| | | |
|---|---|---|
| PER CENT CA5OH(PO4)3 IN STREAM 10 | 90.11 | PER CENT |
| CA5OH(PO4)3 IN STREAM 10. | 412.55 | LBS. |
| MGO IN STREAM 10 | 222.82 | LBS. |
| TOTAL WEIGHT OF STREAM 10 | 697.82 | LBS. |
| PERCENT P2O5 IN STREAM 10 | 24.00 | PER CENT |
| CO2 IN STREAM 14 | 1778.42 | LBS. |
| CO2 IN STREAM 15 | 2980.42 | LBS. |
| FRESH WATER IN STREAM 8 | 149526.90 | GALLONS |
| FRACTION OF STREAM 9 TO STREAM 13 | 0.52 | |
| CO2 IN STREAM 16 | 357.06 | LBS. |
| CACO3 RECOVERED IN STREAM 12 | 810.53 | LBS. |
| FRESH WATER EFFLUENT IN STREAM 17 | 71761.37 | GALLONS |
| CAO MAKE-UP IN STREAM 6 | 0.00 | LBS. |
| MAKE-UP CAO DOSE TO TOTAL CAO DOSE RATIO | 0.00 | |

In the illustration, the system is self-sustaining in lime; in fact, it generates lime because of the hardness of the feed. The model provides for the circumstances of softer waters.

## COMPARISON OF MODEL WITH ANALYTICAL RESULTS

In the laboratory, four one-liter batches of secondary effluent from the Dayton Sewage Plant were treated with lime to remove phosphate. Each liter of effluent was first doped with 10 mg of phosphorus (as ortho-phosphate) to bring phosphorus level to 15.5 mg/l. The sludge collected after treatment of each liter was calcined and reused with the required makeup lime in the next liter of effluent. The laboratory treatment and analysis of the effluents and sludge was the same as that described earlier in this report. In addition, suspended solids and alkalinity of the secondary effluent were determined. Laboratory data and results are presented in Table 21 (refer also to Figure 14).

Final product sludge recovered, after slaking to remove lime, amounted to 591.8 mg of which 61 mg was P. This sludge phosphorus content is derived from the phosphorus content of effluent before and after liming and the number of liters treated. Average phosphorus removal efficiency was 98.4%.

Values of input variables for the model are those shown in the "Average" column in Table 21, except for sludge attrition factor and allowable sludge buildup. Sludge attrition factor was selected at 0.90 (10% loss of sludge solids) as a reasonable figure. Allowable sludge buildup was chosen as 25%. The latter is only incidental to the comparison as it merely affects prediction of certain steady state quantities.

Input to and output from the model are shown in Table 22. Those values that can be compared with experimental values obtained are presented in Table 23. The disparity between actual and predicted results shown in Table 23 indicates that the assumptions for the model require verification and possible modification to improve reliability. However, the model is useful for approximate calculations such as preliminary cost estimates.

Table 21

EFFLUENT QUALITY FROM LABORATORY TREATMENT
OF SECONDARY EFFLUENT FOR PHOSPHATE REMOVAL

| | Batch Number (1 liter each) | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | Avg. |
| *Secondary Effluent Analysis | | | | | |
| Ca Hardness (mg/l Ca) | 93.0 | 93.0 | 93.0 | 93.0 | 93.0 |
| Mg Hardness (mg/l Mg) | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 |
| P (mg/l P) | 15.5 | 15.5 | 15.5 | 15.5 | 15.5 |
| Suspended Solids (mg/l) | 49.4 | 49.4 | 49.4 | 49.4 | 49.4 |
| Alkalinity (mg/l $HCO_3^-$) | 119.0 | 119.0 | 119.0 | 119.0 | 119.0 |
| Fresh Water Analysis | | | | | |
| Hardness (mg/l $CaCO_3$) | | | | | 120.0 |
| **Tertiary Effluent Analysis | | | | | |
| Ca Hardness (mg/l Ca) | 24.0 | 20.0 | 38.0 | 69.0 | 38.0 |
| Mg Hardness (mg/l Mg) | 2.0 | 3.0 | 2.0 | 1.0 | 2.0 |
| P (mg/l P) | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| Treatment Data | | | | | |
| pH -- initial | 7.1 | 7.0 | 7.1 | 7.0 | |
| pH - after sludge + CaO | 11.3 | 11.0 | 11.0 | 11.0 | |
| pH - after $CO_2$ | 9.0 | 9.0 | 9.0 | 8.5 | |
| Lime Dose (mg) | 400 | | | | |
| Sludge Recovery (mg) | 444.9 | | | | |
| Make-up Lime (mg) | | 58.4 | | | |
| Sludge Recovery (mg) | | 599.0 | | | |
| Make-up Lime (mg) | | | 1.4 | | |
| Sludge Recovery (mg) | | | 635.4 | | |
| Make-up Lime (mg) | | | | 43.8 | |
| Sludge Recovery (mg) | | | | 741.2 | |
| SLUDGE BUILD-UP (%) (TOTAL RECYCLE) | 0.0 | 34.6 | 42.8 | 66.6 | |
| SLUDGE RECOVERY (mg) (AFTER SLAKING) | | | | 591.8 | |

*Stream 1 Feed
**Stream 11 Effluent

Table 22

## COMPUTER PREDICTED RESULTS BASED ON ANALYTICAL DATA INPUT

**INPUT VARIABLES**

| | |
|---|---|
| CA CONTENT OF STREAM I (MG/L) AS CA | 93.00 |
| CA CONTENT OF STREAM II (MG/L) AS CA | 38.00 |
| MG CONTENT OF STREAM I (MG/L) AS MG | 20.00 |
| MG CONTENT OF STREAM II (MG/L) AS MG | 2.00 |
| P CONTENT OF STREAM I (MG/L) AS P | 15.50 |
| P CONTENT OF STREAM II (MG/L) AS P | 0.25 |
| SUSPENDED SOLIDS CONTENT OF STREAM I (MG/L) | 49.40 |
| ATTRITION FACTOR | 0.90 |
| BICARBONATE CONTENT OF STREAM I AS HCO3- (MG/L) | 119.00 |
| HARDNESS OF FRESH WATER AS CACO3 (MG/L) | 120.00 |
| SLUDGE BUILD-UP ALLOWED (0-1) | 0.25 |

**********

STEADY STATE FOR 1 MILLION GALLONS WITH 400 MG/L LIME DOSE IN STREAM 1
ASSUMING A. ALL P AS CA5OH(PO4)3 IN STREAM 10
B. 75 PER CENT SUSPENDED SOLIDS VOLATILE

KX= WEIGHT IN LBS OF STREAM 4 AFTER X CYCLES WITH TOTAL RECYCLE
LX= PER CENT SLUDGE WEIGHT BUILD-UP IN STREAM 4 AFTER X CYCLES WITH TOTAL RECYCLE

| | | | LBS. | | PER CENT |
|---|---|---|---|---|---|
| CYCLE NUMBER | 1 | KX | 4161.91 | LX | 0.00 |
| CYCLE NUMBER | 2 | KX | 5319.62 | LX | 27.81 |
| CYCLE NUMBER | 3 | KX | 6477.33 | LX | 55.63 |
| CYCLE NUMBER | 4 | KX | 7635.04 | LX | 83.45 |
| CYCLE NUMBER | 5 | KX | 8792.75 | LX | 111.26 |
| CYCLE NUMBER | 6 | KX | 9950.46 | LX | 139.08 |
| CYCLE NUMBER | 7 | KX | 11108.17 | LX | 166.90 |
| CYCLE NUMBER | 8 | KX | 12265.88 | LX | 194.71 |
| CYCLE NUMBER | 9 | KX | 13423.59 | LX | 222.53 |
| CYCLE NUMBER | 10 | KX | 14581.31 | LX | 250.35 |

**********

**OUTPUT**

| | | |
|---|---|---|
| PER CENT CA5OH(PO4)3 IN STREAM 10 | 55.59 | PER CENT |
| CA5OH(PO4)3 IN STREAM 10 | 629.15 | LBS. |
| MGO IN STREAM 10 | 224.20 | LBS. |
| TOTAL WEIGHT OF STREAM 10 | 946.12 | LBS. |
| PERCENT P2O5 IN STREAM 10 | 28.23 | PER CENT |
| CO2 IN STREAM 14 | 2140.46 | LBS. |
| CO2 IN STREAM 15 | 2855.65 | LBS. |
| FRESH WATER IN STREAM 8 | 151768.53 | GALLONS |
| FRACTION OF STREAM 9 TO STREAM 13 | 0.63 | |
| CO2 IN STREAM 16 | 274.78 | LBS. |
| CACO3 RECOVERED IN STREAM 12 | 561.39 | LBS. |
| FRESH WATER EFFLUENT IN STREAM 17 | 55226.27 | GALLONS |
| CAO MAKE-UP IN STREAM 6 | 0.00 | LBS. |
| MAKE-UP CAO DOSE TO TOTAL CAO DOSE RATIO | 0.00 | |

Table 23

SUMMARY OF THE COMPARISON OF ACTUAL AND PREDICTED RESULTS OF PHOSPHATE SLUDGE ENRICHMENT

| | Predicted By Model | Actual From Analysis |
|---|---|---|
| A. Sludge Recovery | | |
| 1. weight | 455 mg/4 l | 591.8 mg/4 l |
| 2. P content as % $P_2O_5$ | 28.23% | 23.60% |
| % Ca $OH(PO_4)_3$ | 66.51% | 55.40% |
| B. $CaCO_3$ Recovery | | |
| 1. weight | 269.1 mg/4 l | 267.0 mg/4 l |
| C. Sludge Buildup-Total Recycle | | |
| 1. sludge at Point 4 (Figure 14) | | |
| one cycle | 500 mg | 445 mg |
| two cycles | 640 mg | 599 mg |
| three cycles | 778 mg | 635 mg |
| four cycles | 918 mg | 741 mg |

## SECTION VI

## THE MAGNESIUM CONTENT OF SLUDGE

The magnesium content of the lime sludge may be worth considering. For phosphate sludge to be competitive with phosphate rock, it must contain about 30% $P_2O_5$. Beneficiation of phosphate sludge by means of slaking out the CaO will yield, under favorable conditions, sludge containing about 27% $P_2O_5$ (on a dry basis). On the basis of $P_2O_5$ content, the phosphate sludge might be sold as a low-grade phosphate rock. There is, however, a major difference between phosphate rock and phosphate sludge. The sludge, in our study, contains about 25% MgO compared to 0.2% MgO for phosphate rock. The presence of such a large MgO content will require greater $H_2SO_4$ consumption to produce a pound of $P_2O_5$ (5.4 lb. $H_2SO_4$ for the sludge and 2.3 lb. $H_2SO_4$ for the rock). Furthermore, the $MgSO_4$ resulting from the digestion with $H_2SO_4$ is very soluble and its removal from produce $H_3PO_4$ may be a problem.

Although the presence of MgO is a nuisance in the recovery of $H_3PO_4$, by dilution of the phosphate value, it might be turned into an advantage. Recent market surveys have indicated that the use of Mg will double in two to three years. The use of Mg in 1969 will be close to 140,000 tons. Referring to earlier comparisons where in Chicago the daily sewage flow is estimated to be 1.3 bgd, the quantity of Mg precipitated per year, for 15 mg/l Mg in the waste water, will be:

$$(1.3 \times 10^9)(365)(15 \times 10^{-6}) \quad \frac{8.33}{2000} = 29{,}600 \text{ tons/year}$$

This represents about 10% of the total projected Mg requirements for 1972.

Figure 15 represents a potential process for the recovery of $MgCl_2$ and $H_3PO_4$ from the lime-phosphate sludge. Again, there arises the question of where the processing would occur. Nevertheless, referring to Figure 15, dry phosphate sludge (after beneficiation) is mixed with sulfuric acid, water and calcium chloride forming a slurry of calcium sulfate and phosphate in a solution of magnesium chloride. The sulfate and phosphate are filtered off and treated with dilute sulfuric acid. Here a slurry of calcium sulfate in phosphoric acid is formed from which the sulfate is separated by filtration. $MgCl_2$ can be concentrated, dried and sold to



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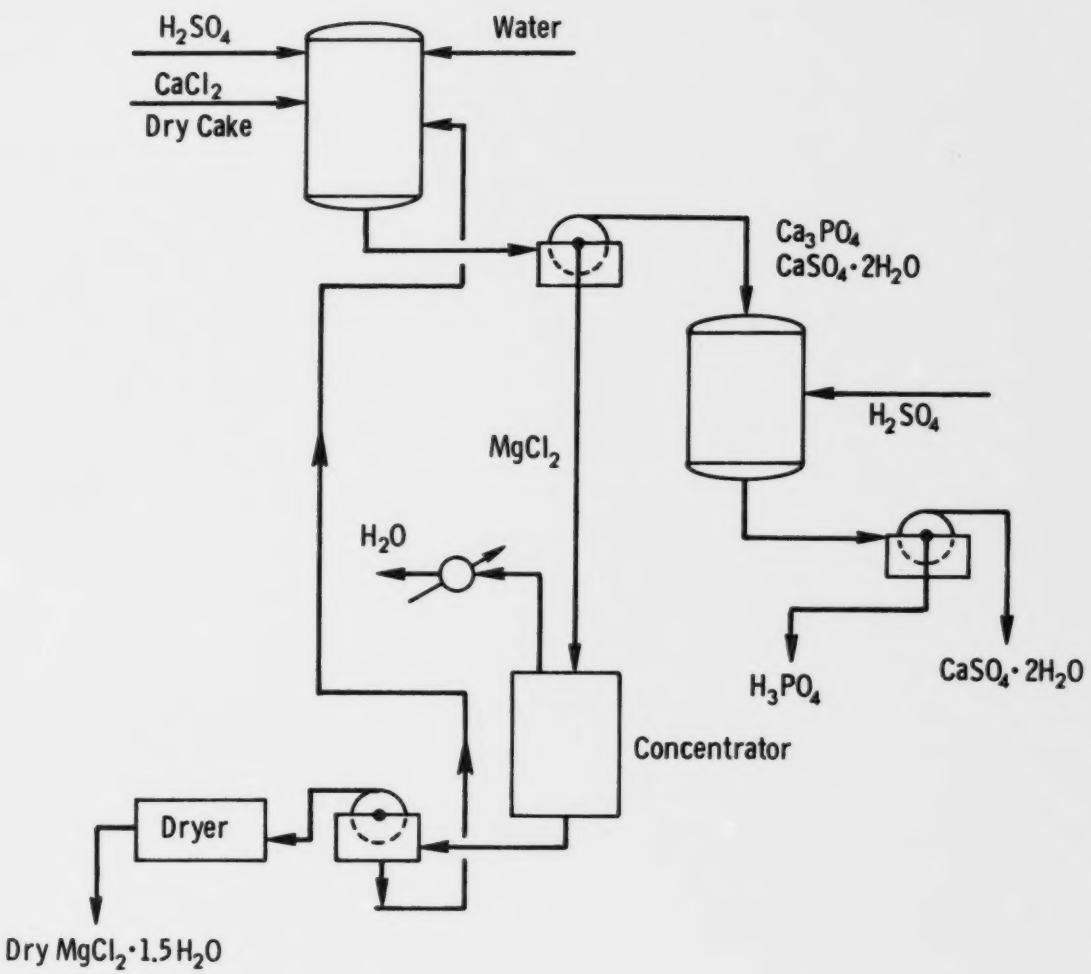


Figure 15. Potential Process for Recovery of Both Magnesium and Phosphorus Values from Sludge

Mg manufacturers or possibly converted to Mg and $Cl_2$ at the phosphoric acid plant.

The process outlined above is a preliminary concept. It shows only that a valuable product can be recovered from phosphate sludge. Further studies would be required to produce definitive design data.

Considering only raw materials, required in the recovery of the magnesium content, a ton of beneficiated sludge, with the composition indicated in Table 22 would have a potential value of about $65-70. The same amount, and composition, of sludge based on phosphate value would be worth about $3.00. A detailed economic evaluation would be required to determine the potential profitability of this approach.

The materials costs used in this preliminary look at the process are given below.

| | |
|---|---|
| $H_2SO_4$ 60° Be (100% basis) | $ 26.90/ton |
| $CaCl_2$ 77-88% flake (100% basis) | 39.50/ton |
| Dry Sludge | 16.00/ton |
| $MgCl_2$ anhd. 92% (100% basis) | 255.00/ton |
| $H_3PO_4$ ag. grade (100% basis) | 90.00/ton |

The following composition of beneficiated dry sludge was used in the process estimation.

| | | |
|---|---|---|
| For a 1,000,000 gpd basis: | $Ca_5(OH)(PO_4)_3$ | 404 lb |
| | MgO | 218 lb |
| | Inerts | 278 lb |
| | | 900 lb/day |

## SECTION VII

## ECONOMIC EVALUATION OF PHOSPHATE ENRICHMENT

Preliminary estimates of the incremental capital and operating costs for phosphate enrichment by the slaking process are shown in Table 23. The material balance is based on the data in Table 21. The process was considered as an additional part of an existing water reclamation plant so that only the incremental section shown in Figure 16 was considered. Estimates are based on chemical industry cost estimating practice and thus may not be directly comparable to estimates derived from civil or municipal cost estimating procedures. Nevertheless, within themselves, the costs have comparative meaning.

For each of three daily capacities, namely 1-, 10-, and 100-million gpd, three cases were established, indicated in Figure 16, as follows:

Case 1 -- All steps are included (all of Figure 16) required to produce dry apatite and dry calcite.

Case 2 -- Calcite recovery after apatite removal is excluded. Only dry apatite is produced.

Case 3 -- Same as Case 2 except that apatite cake is produced wet (about 50% solids).

The assumptions involved in the cost estimates and a detailed example are shown in the Appendix.

Table 24

COMPARATIVE COST SUMMARY FOR VARIOUS CASES OF PHOSPHATE ENRICHMENT PROCESS

| | Capital Cost | | Purchased | Operating Cost | |
|---|---|---|---|---|---|
| | $ | $/M gal | Equip.Cost, $ | Annual $ | ¢/M gal |
| Case 1 - a | 211,300 | 211.00 | 74,750 | 90,550 | 27.5 |
| b | 562,000 | 56.00 | 201,900 | 228,800 | 7.0 |
| c | 2,049,300 | 20.50 | 794,900 | 769,700 | 2.5 |
| Case 2 - a | 148,100 | 148.00 | 51,950 | 76,800 | 23.0 |
| b | 390,400 | 39.00 | 144,400 | 149,700 | 4.5 |
| c | 1,574,000 | 15.70 | 594,750 | 608,400 | 1.9 |
| Case 3 - a | 58,400 | 58.00 | 20,500 | 12,800 | 4.0 |
| b | 162,100 | 16.00 | 56,400 | 39,200 | 1.2 |
| c | 670,000 | 6.70 | 230,750 | 181,900 | 0.6 |



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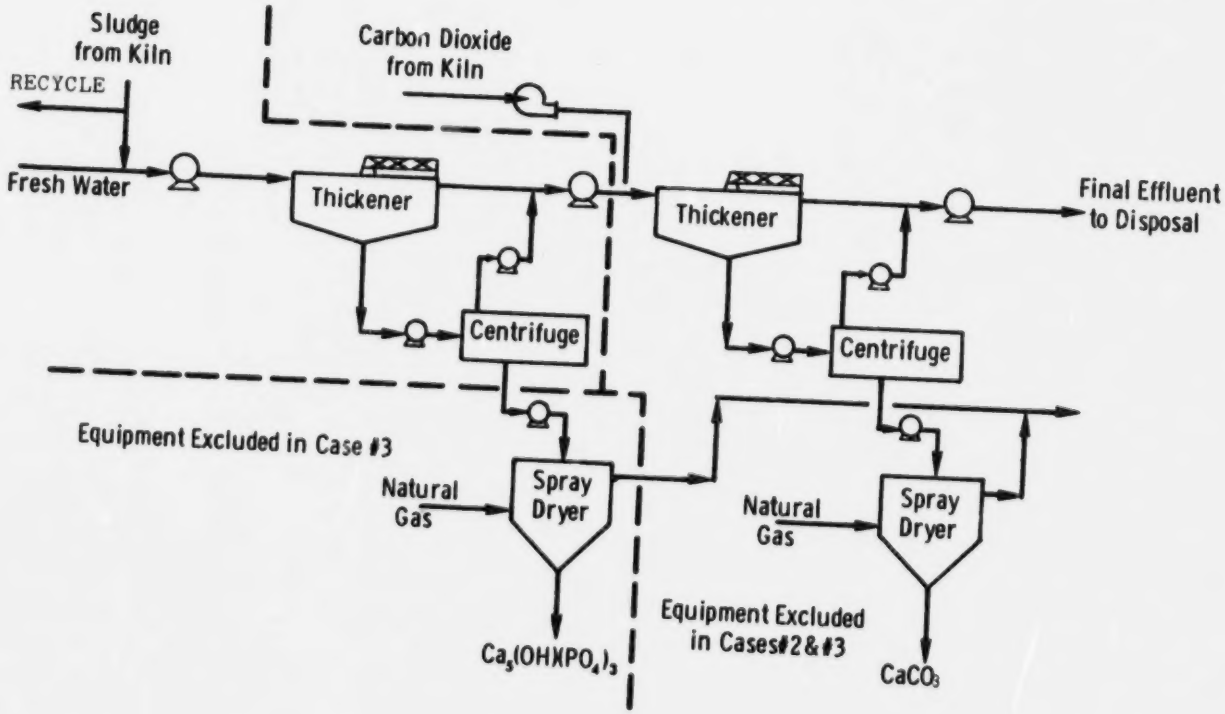


Figure 16. Preliminary Schematic Flow Diagram for Cost Estimating

It is, perhaps, prudent to emphasize here that these are very preliminary cost estimates whose primary value is twofold at the moment. First, they give an indication of the effect of capacity on cost; second, they indicate the value of the product compared to the cost of production. The latter comparison is shown in Table 25 below.

Table 25

COMPARISON OF PHOSPHATE PRODUCT VALUE AND PRODUCTION COST

| Capacity mgd | Product tons/yr | Product Value* $/yr | Operating Cost** $/yr |
|---|---|---|---|
| 1 | 136 | 880 | 12,800 |
| 10 | 1,360 | 8,800 | 39,200 |
| 100 | 13,600 | 88,000 | 181,900 |

*at $6.50/short ton
**cheapest case in Table 22

While it is apparent that the product value might defray a small portion of the operating cost, the great discrepancy between product value and production cost gives pause to wonder. Figure 17 shows what the plant capacity would have to be to "break even" with product price at $6.50/short ton; or, what the product price would have to be to break even at the capacities used in the cost estimate.

Part of the reason for low product value is found in the following. Recent prices (Oct. 31, 1969) for Florida phosphate rock are shown in Table 26.

These data indicate clearly that a premium price is paid for higher $P_2O_5$ concentrations. Extrapolating this relationship, a material containing 25% $P_2O_5$ would be worth only about $5.20 per ton of $Ca_3(PO_4)_2$ and a material containing only 18-19% $Ca_3(PO_4)_2$ would not have any price as a phosphate source.

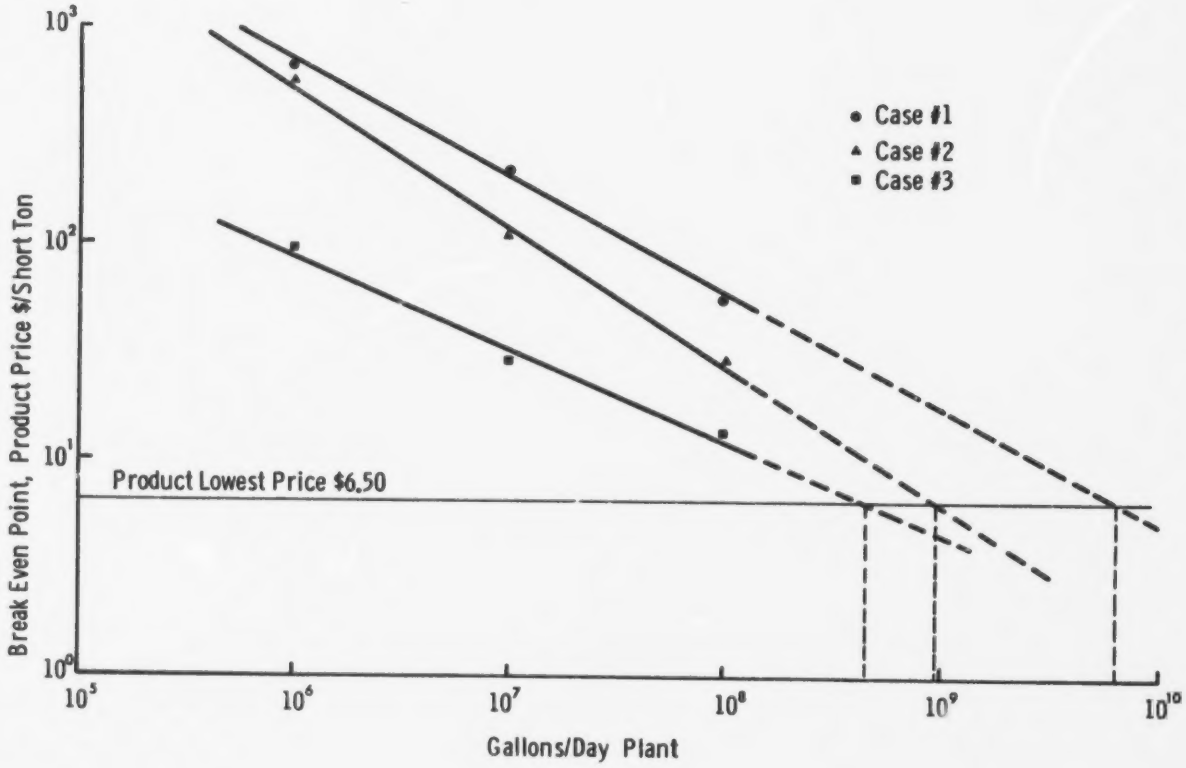


Figure 17. Effect of Plant Size on Potential Product Value

Table 26

CURRENT PRICES FOR PHOSPHATE ROCK

| BPL* | $\%P_2O_5$ (avg.) | $/Short Ton** |
|---|---|---|
| 66-68 | 30.7 | 6.50 |
| 68-70 | 31.6 | 7.50 |
| 70-72 | 32.5 | 8.15 |
| 74-75 | 34.1 | 9.20 |
| 76-77 | 34.8 | 10.20 |

*BPL = bone phosphate of lime value, which is equivalent to the $Ca_3(PO_4)_2$ content

**FOB point of production

Reference to Table 21 reveals that the product stream (Stream 10) contains only 23-25% $P_2O_5$ because of the diluting effects of roughly 25% MgO present and the form in which the phosphate probably exists. Consequently, in areas where the magnesium content is appreciable, even though the sludge phosphate content can be considerably enriched, it may still not be possible to achieve a product with value as a "phosphate rock." Figure 18 shows the effect of phosphorus content in secondary effluent (to phosphate removal process) on the $P_2O_5$ level in the product from beneficiation, assuming a constant magnesium concentration as in Table 21 (Stream 1).

## COMPARATIVE COST ESTIMATES FOR COMBINATION PROCESSES

Not only are there several variations possible for recovery of lime and phosphate but there are also several combinations for liming for phosphate removal with and without lime or phosphate recovery. These various possibilities are shown in order of increasing complexity in Figures 19 through 23. To a large extent, these operations are based on our understanding of operations at the Lake Tahoe plant (Ref. 16) and, essentially, consist only of those steps required to remove phosphate and recover (or not) lime and/or phosphate.

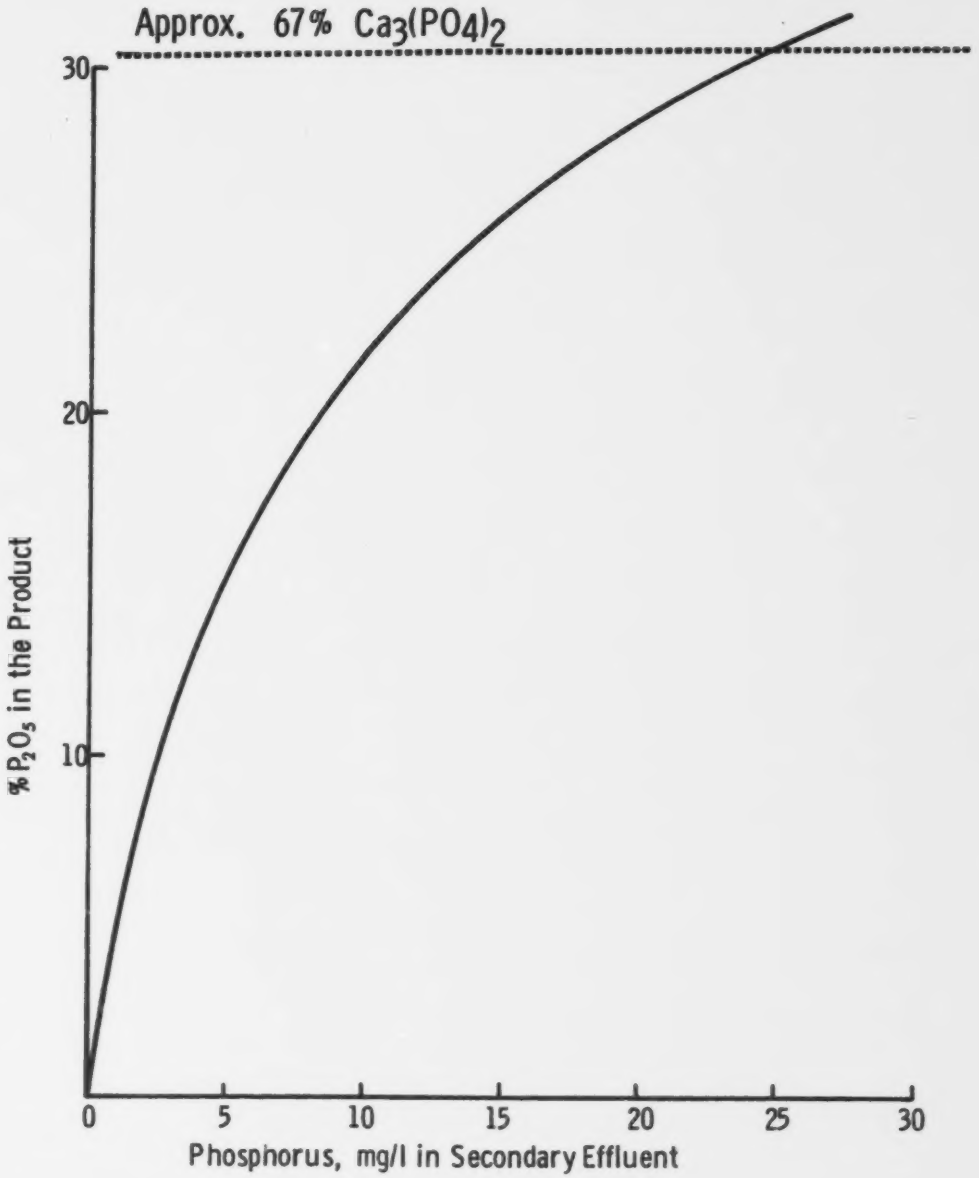


Figure 18. Effect of Phosphorus Concentration in the Feed on Phosphorus Concentration in the Product

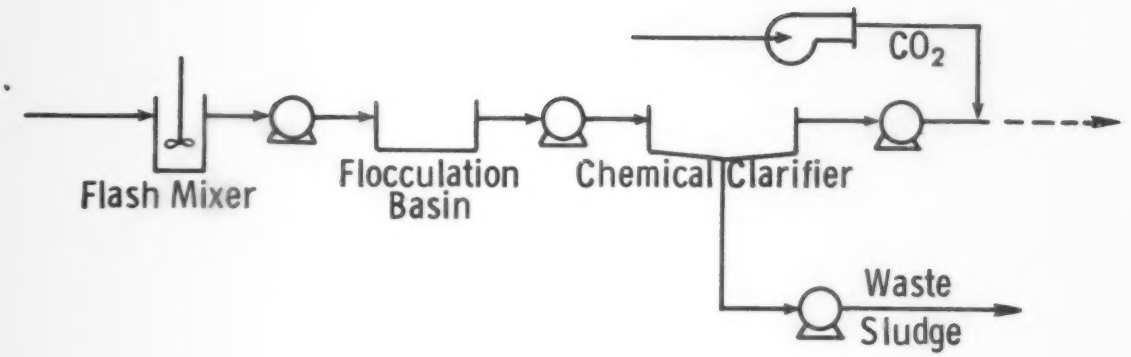


Figure 19. Liming for Phosphate Removal.
Case 1: NO Recovery

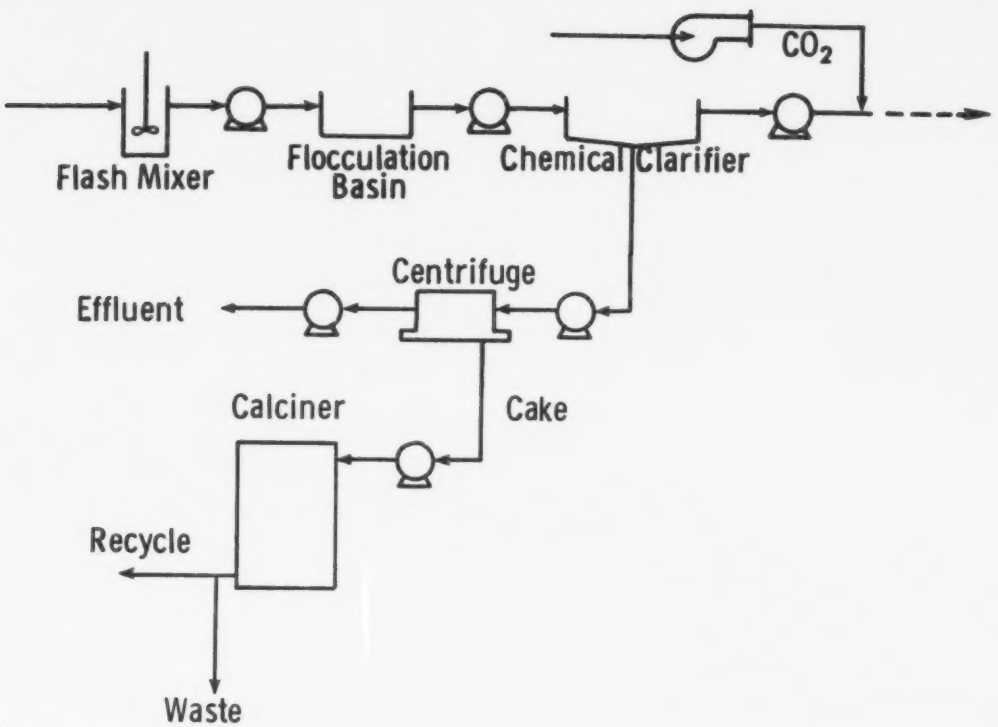


Figure 20. Liming for Phosphate Removal.
Case 2. Partial Lime Recovery

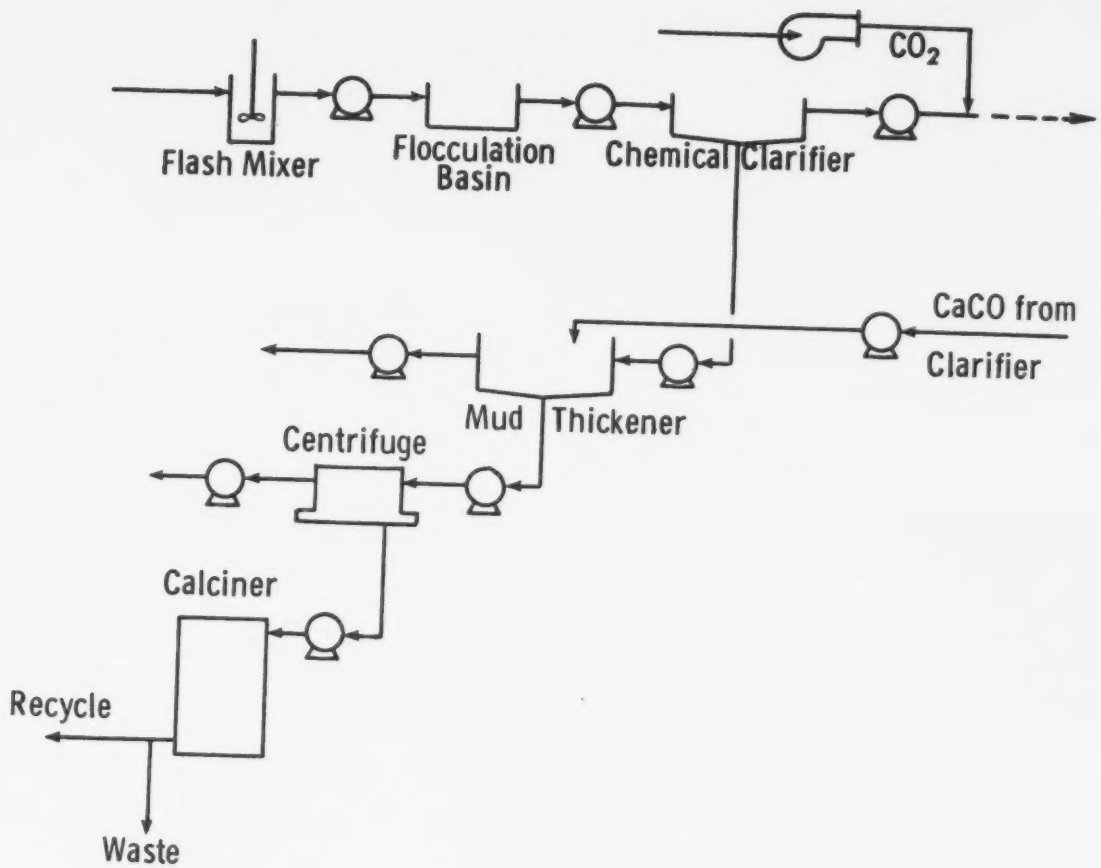


Figure 21. Liming for Phosphate Removal.
Case 3: Full Lime Recovery

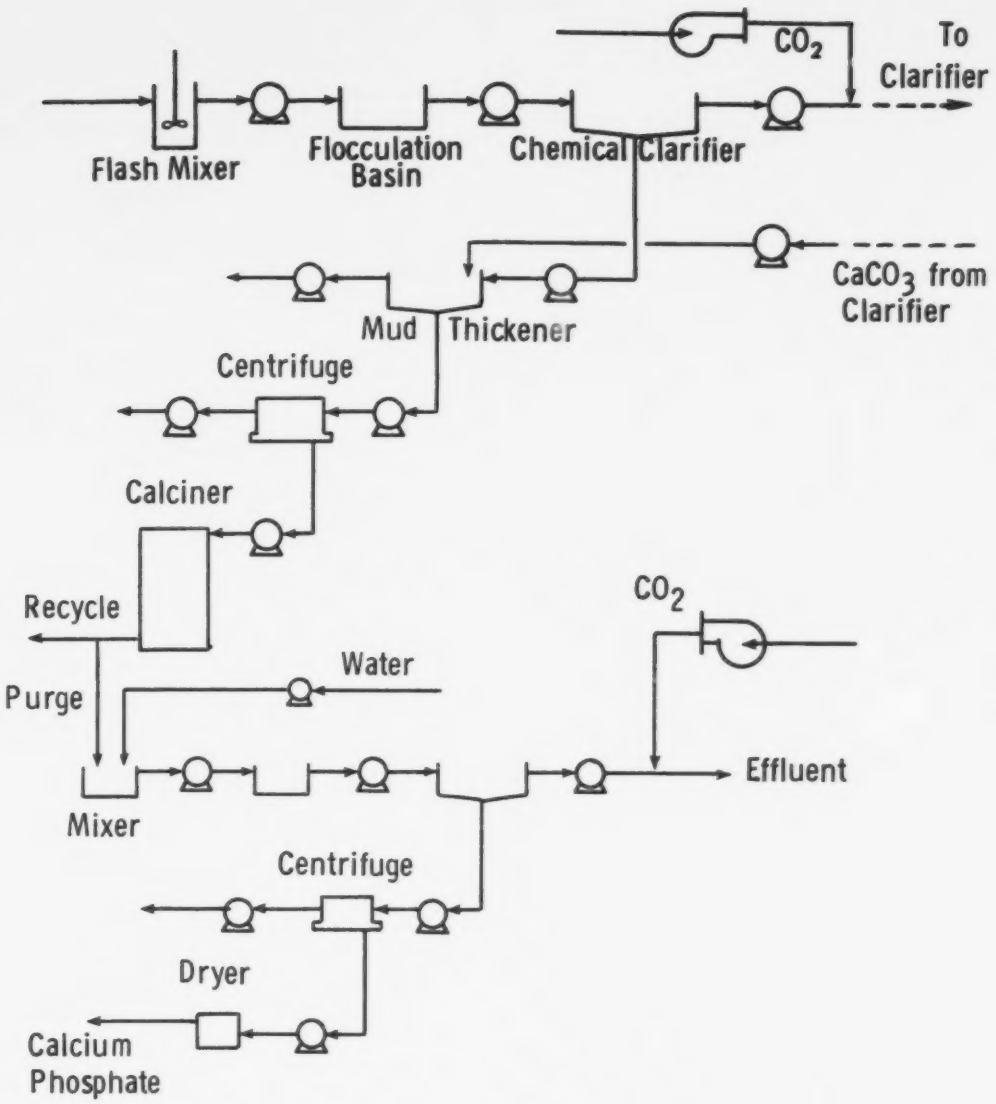


Figure 22. Liming for Phosphate Removal.
Case 4: Phosphate and Partial Lime Recovery

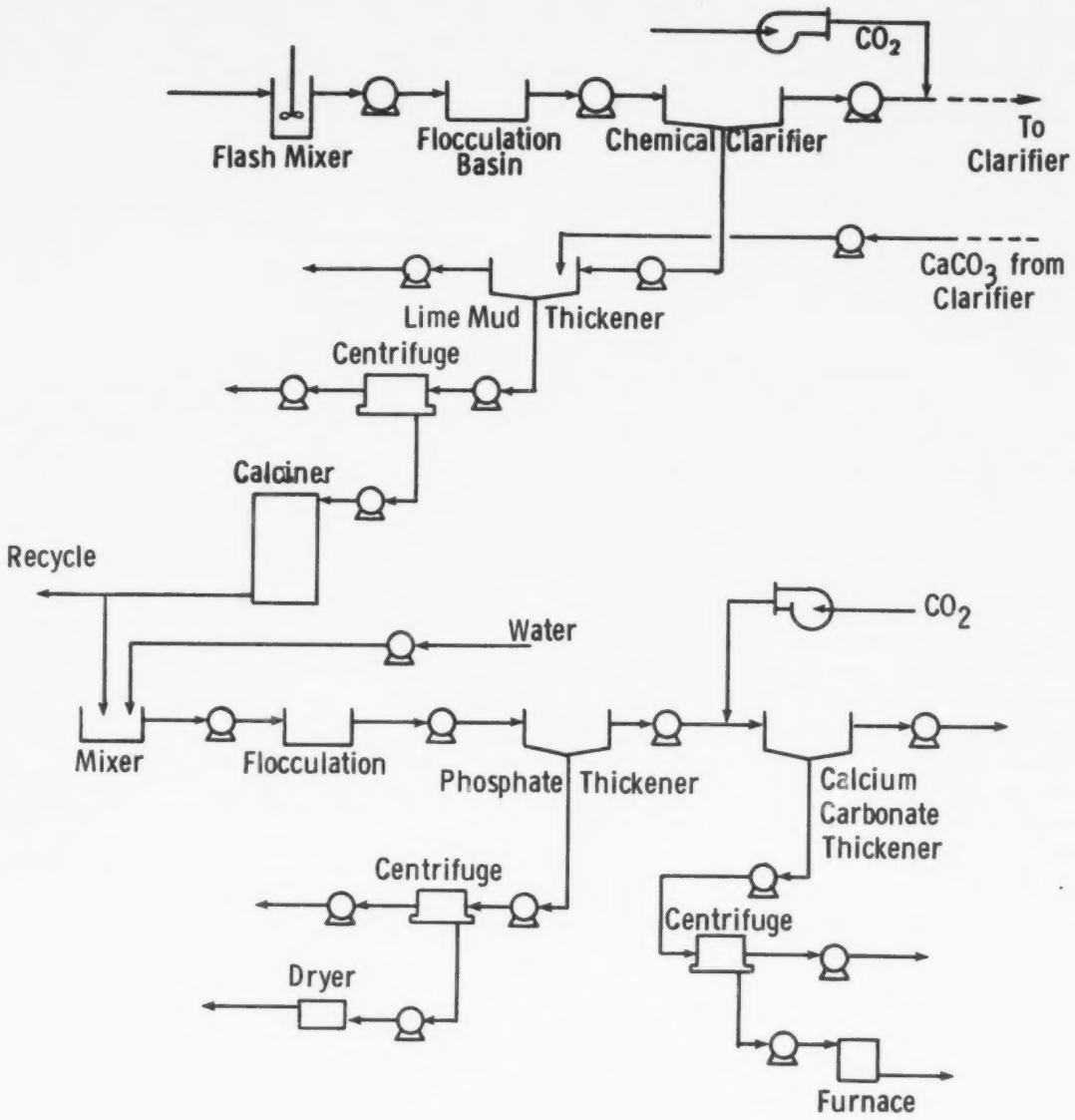


Figure 23. Liming for Phosphate Removal.
Case 5: Full Recovery of Lime and Phosphate

The first case, Figure 19, consists only of liming secondary effluent for phosphate removal and wasting of all lime. Effluent is carbonated for pH control. Here we consider $CO_2$ available from a combustion process, as, for example, at Tahoe from primary sludge incineration. Otherwise, packaged $CO_2$ may be required.

In Case 2, some lime is recovered and recycled. The amount of such recovery, in practice, would depend upon carbonate/bicarbonate hardness of the feed. In our studies we have, throughout, employed composition as given in Table 16. The relatively high bicarbonate content suggests recovery of a portion of the lime added as calcium carbonate in the phosphate sludge. No attempt is made in Case 2 to recover soluble calcium in the effluent. Carbonation is only for pH control. Carbon dioxide for carbonation may come from the calciner or from a sludge incinerator as previously mentioned. There is no effort to justify the cost of the calciner in this case even though, probably, less than 50% of added lime may be recovered. The major intent is to show added cost through added process complexity.

In Case 3, effort is made to recover all lime and two-thirds recovery is assumed. The flocculation basin and clarifier for calcium carbonate are not included in these estimates. In the general case they would be, but our orientation here was strongly aligned with Tahoe operation and these flocculation and clarification operations at Tahoe were, nominally, in a downstream system (i.e., ammonia stripping). This does not change the relative costs significantly, considering that these are preliminary estimates. This case probably represents a practical optimum.

Case 4 not only represents lime recovery and reuse but also by-product phosphate production. Here, though, there is lime wastage in the effluent from the phosphate beneficiation operation.

By comparison, Case 5 attempts to recover <u>all</u> lime and produces by-product phosphate.

Table 26 summarizes comparative costs for all the cases and flow rates. Assumptions made for the calculations and a detailed example are given in the Appendix G.

It is interesting to compare Case 1-a, in Table 24, with Case 5 at $10^6$ GPD flow in Table 27. The former approximates only the incremental cost of beneficiation while the latter approximates the total cost of the tertiary step of phosphate removal plus beneficiation. It appears, considering the margin in these estimates, that beneficiation alone can represent roughly half the total cost of removing and recovering phosphate.

Case 5 might be designed without the second furnace. The recovered calcium carbonate sludge from the second calcium carbonate thickener could be recycled back to the first furnace and calcined along with lime mud. However, the size of the first furnace would have to be reevaluated. It is obvious that this arrangement would not result in significantly lower direct operating cost but only in lower capital cost requirement.

It is quite evident that the minimum treatment of the sludge is the least cost option. Of the other options, Case 3 is the least costly. Attempts to recover phosphate and lime cause a considerable increase in treatment cost.

Cost of transporting lime to and removal of sludge from the plant site have not been considered because they are extreme functions of local situations. However, the total bulk of materials to be transported in and out of the plant is the same for Cases 3, 4 and 5. Thus, Case 4 and 5 can make no claim for lower transportation costs than Case 3 and the latter remains as considerably more economical than Cases 4 and 5.

It can be concluded from these calculations that the most economical approach to phosphate removal is continuous use of fresh with no attempt to recover sludge for recycle purposes. The major difficulty with this approach would lie in the cost of transportation and nuisance factors involved in disposal of wet sludge containing some organic solids.

The next most economical approach is Case 3 which recovers and recycles lime. Beyond this, the added cost for recovery of phosphate and excess lime (above process needs) cannot be justified.

Table 27

CAPITAL REQUIREMENTS AND OPERATING COST FOR MODIFIED THERMAL BENEFICIATION

| Flow Rate GPD | Case No. | Purchased Equipment $ | Capital Requirement $ | Capital Requirement $/1000 GPD | Operating Cost $/Yr. | Operating Cost ¢/1000 G |
|---|---|---|---|---|---|---|
| $10^6$ | 1 | 24,960 | 91,470 | 91.47 | 27,930 | 8.46 |
| $10^6$ | 2 | 101,280 | 456,040 | 456.04 | 151,300 | 45.85 |
| $10^6$ | 3 | 92,700 | 418,060 | 418.06 | 136,170 | 41.26 |
| $10^6$ | 4 | 107,450 | 508,040 | 508.04 | 195,300 | 59.18 |
| $10^6$ | 5 | 124,530 | 576,450 | 576.45 | 208,400 | 63.15 |
| $10^7$ | 1 | 88,790 | 318,480 | 31.85 | 156,510 | 4.74 |
| $10^7$ | 2 | 522,370 | 2,199,200 | 219.92 | 645,880 | 19.57 |
| $10^7$ | 3 | 471,100 | 1,976,000 | 197.60 | 527,410 | 15.98 |
| $10^7$ | 4 | 512,600 | 2,183,300 | 218.33 | 656,750 | 19.90 |
| $10^7$ | 5 | 587,350 | 2,497,100 | 249.71 | 715,230 | 21.67 |
| $10^8$ | 1 | 648,180 | 2,220,300 | 22.20 | 1,366,450 | 4.14 |
| $10^8$ | 2 | 4,104,160 | 16,554,400 | 165.54 | 5,208,700 | 15.78 |
| $10^8$ | 3 | 3,188,600 | 12,797,700 | 127.98 | 3,707,650 | 11.24 |
| $10^8$ | 4 | 3,353,200 | 13,603,900 | 136.04 | 3,876,490 | 11.75 |
| $10^8$ | 5 | 3,741,100 | 15,041,100 | 150.41 | 4,177,020 | 12.66 |

## SECTION VIII

## ACKNOWLEDGMENTS

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# APPENDIX A

## THERMAL BENEFICIATION

### Preparation of New Lebanon Sludge

To synthesize a high phosphate content lime sludge, 7 liters of sewage from the New Lebanon, Ohio treatment plant were treated with 1500g $NaH_2PO_4$, 192g CaO, and 339g NaOH. The pH of this solution was lowered from 10.5 to 8.3 by carbonation. The wet cake of lime sludge resulting from filtering the treated sewage was used for thermal beneficiation experiments.

### Preparation of Lake Tahoe Sludge

Lake Tahoe sludge sample #2 was the wet cake of sludge obtained after centrifuging. Calcination of this sludge at 950°C for 90 minutes resulted in a non-caking, white solid. Lake Tahoe sludge sample #4 was lime sludge from the calciner. This sample was also a finely divided, white solid.

APPENDIX A (cont'd)

Table A-1

RESULTS OF PHOSPHORUS ANALYSIS ON SOLID SLUDGE SAMPLES

| Sample Treatment | Sample # | %P |
|---|---|---|
| New Lebanon-Slaked, in cold water. | 1. initial | 12.57 |
| | 2. fines | 14.72 |
| | 3. residue | 14.57 |
| New Lebanon-Slaked, in boiling water for 2 hours. | 4. fines | 15.44, 15.26 |
| | 5. residue | 15.65 |
| Lake Tahoe #4 | 6. initial | 2.66, 2.62 |
| | 7. fines | 2.38, 2.31 |
| | 8. residue | 2.19, 2.22 |
| Lake Tahoe #2 | 9. initial | 1.70, 1.71 |
| | 10. fines | 2.33 |
| | 11. residue | 2.32 |

## APPENDIX B

## CARBONATION

### Preparation of Column

Thirty grams of uncalcined Lake Tahoe sludge were packed in a 11.1 cm x 2.5 cm glass column. The dry cake of sludge was not finely divided. Loose packing allowed the free flow of liquid.

Table B-1

RESULTS OF PHOSPHORUS ANALYSIS ON SOLID SLUDGE SAMPLES

| Sample | %P |
|---|---|
| Lake Tahoe #3 (initial) | 7.36, 7.27 |
| Lake Tahoe #3 (after removal of $CaCO_3$ by dissolution) | 8.11 |

APPENDIX B (cont'd)

Table B-2

| Cycle # | Volume (liters) | Wt. $CaCO_3$ Recovered (grams) |
|---|---|---|
| 1 | 0.60 | |
| 2 | 1.00 | 1.53 |
| 3 | 1.10 | 0.55 |
| 4 | 1.04 | 0.61 |
| 5 | 1.00 | 0.41 |
| 6 | 1.00 | 0.39 |
| 7 | 1.00 | 0.48 |
| 8 | 1.00 | 0.44 |
| 9 | 1.00 | 0.44 |
| 10 | 1.00 | 0.45 |
| 11 | 1.00 | 0.49 |
| 12 | 1.00 | 0.30 |
| 13 | 1.00 | 0.32 |
| 14 | 1.00 | 0.50 |
| Total | 13.74 | 6.91 |

AVG. Recovery = 0.50 g $CaCO_3$/liter of carbonated water

Enriched Sludge Recovered From Column = 24.8g

# APPENDIX C

# SLAKING

## SIMULATED CALCINED SLUDGE PREPARATION

An aqueous unsaturated solution containing 80 g of $Na_4P_2O_7 \cdot 10\ H_2O$ was mixed with an unsaturated aqueous solution containing 40 g of $CaCl_2$. The resulting insoluble $Ca_2P_2O_7 \cdot 5\ H_2O$ was filtered from the mixture and heated at 1000°C for 2 hours to simulate calcining conditions. After crushing, this phosphate material was mixed with CaO to give simulated calcined sludges containing 5, 10, 15, 20, 25, and 30% $Ca_2P_2O_7$.

## SLAKING METHOD AND EFFLUENT ANALYSIS

Five gram samples of each of the simulated sludges were slaked with 1 liter of deionized water. The hardness of each respective liter of slaking water was determined, after filtration, with Hach Total Hardness Test Kit No. HA-71. The hardness of the water was assumed to equal the amount of Ca removed from the sludge. This loss in sludge weight as CaO was used to calculate the increase in $Ca_2P_2O_7$ percent in the remaining sludge. Each effluent was also tested with the Hach Ortho-Phosphate Test Kit No. PO--14. The absence of phosphate

in each effluent showed that the Ca in the slaking water was all due to the dissolution of lime. After carbonation and filtration of the effluent. The hardness was again measured. The difference in hardness before and after carbonation was used to calculate Ca removal efficiences.

Table C-1

| Sludge $Ca_2P_2O_7$ Content | | Ca Removal Efficiency | |
|---|---|---|---|
| Initial, % | Final, % | From % to % | |
| 5 | 7.0 | 46.5 | 50.0 |
| 10 | 14.1 | 62.7 | 68.6 |
| 15 | 21.1 | 53.5 | 57.5 |
| 20 | 28.1 | 62.7 | 68.6 |
| 25 | 35.0 | 46.5 | 50.0 |
| 30 | 42.2 | 68.6 | 73.6 |

## PROCEDURE FOR PHOSPHATE REMOVAL WITH LIME AND SLUDGE ENRICHMENT BY SLAKING

The following procedure was used in experiments 1, 2, and 3 except where otherwise noted.

1. Treat 4 liters of secondary effluent with $NaH_2PO_4$ equivalent to the addition of 10 mg of P per liter (Experiment 3 only).

2. After measuring the pH of one liter of secondary effluent, add 400 mg of lime to it, mix for five minutes, measure pH again, and filter.

3. Carbonate filtrate to pH ~9, filter again and add the $CaCO_3$ recovered to the phosphate residue recovered in the previous step.

4. Calcine the combined residues at 1800°C for 1-1/2 hours and after cooling in a desiccator, weigh the calcined sludge.

5. After measuring the pH of the second liter of secondary effluent, add the calcined sludge and enough lime to it to raise the pH to 11.

6. Again, mix for five minutes, and filter.

7. Repeat steps 3 through 6 for each experiment until 4 liters of secondary effluent have been treated, i.e. total sludge recycle three times in each experiment.

## SLUDGE AND EFFLUENT ANALYSIS

| | |
|---|---|
| 1. Ca Hardness | Determined in all effluents by titration with standard CDTA (Disodium dihydrogen 1,2-cyclohexanediaminetetraacetate) using 8N KOH (2 drops/10 ml) for pH control with CalVer II indicator (Hach Chemical Co.) giving a red to blue end-point. |
| 2. Mg Hardness | Determined by calculation as difference between Ca hardness and total hardness. |

| | |
|---|---|
| 3. Total Hardness | Determined by titration with standard CDTA, buffered to pH 10 using Eriochrome Black T indicator for a red to blue end-point. |
| 4. Phosphate in Effluent | To 5 ml of sample, add 3 drops of ammonium molybdate solution (Hach Chemical Test Kit No. PO-14) and 0.18 g of StannoVer powder (Hach Chemical - same kit) mix and allow 10 minutes for color development. Then, measure % transmittance on a B&L Spectrometer 20 set at 690 mμ using a red filter. Compare reading to a standard curve. |
| 5. Phosphate in Sludge | (Final sludge of experiment 1 only) by method of Goudie and Rieman. |
| 6. Suspended Solids in Secondary Effluent | (Experiment 3 only) determined by filtering secondary effluent through glass-fritted filtering crucible with medium porosity and drying at 105°C for 48 hours. The difference in weight of the crucible before and after filtering is used to calculate the suspended solids content. |

7. Alkalinity of Secondary Effluent — (Experiment 3 only) determined by titration of effluent with standard HCl to a methyl orange end-point.

Reported Results

1. Ca Hardness reported as mg/l Ca

2. Mg hardness reported as mg/l Mg

3. $PO_4$ content reported as mg/l $PO_4^{\equiv}$ (experiments 1 and 2)
   $PO_4$ content reported as mg/l P (experiment 3)

4. Suspended solids reported as mg/l (experiment 3 only)

5. Alkalinity reported as mg/l $HCO_3^-$ (experiment 3 only)

6. Fresh water hardness reported as mg/l $CaCO_3$ (experiment 3 only)

Table C-2

EFFLUENT ANALYSIS FOR EXPERIMENTS 1 AND 2

| Experiment Number | Cycle (1 liter each) | Feed* mg/l | | | Effluent* mg/l | | | Effluent pH |
|---|---|---|---|---|---|---|---|---|
| | | Ca | Mg | $PO_4$ | Ca | Mg | $PO_4$ | |
| 1 | 1 | 78 | 13 | 18.4 | 77 | 6 | 1.75 | 8.7 |
| | 2 | 78 | 13 | 18.4 | 81 | 18 | 2.88 | 8.0 |
| | 3 | 78 | 13 | 18.4 | 43 | 17 | <1.0 | 9.0 |
| | 4 | 78 | 13 | 18.4 | 23 | 6 | <1.0 | 9.2 |
| 2 | 1 | 93 | 4 | 16.5 | 56 | 3 | <1.0 | 8.9 |
| | 2 | 93 | 4 | 16.5 | 71 | 1 | <1.0 | 8.5 |
| | 3 | 93 | 4 | 16.5 | 33 | 3 | <1.0 | 9.2 |
| | 4 | 93 | 4 | 16.5 | 27 | 1 | <1.0 | 9.0 |

*Feed, stream - 1

Effluent, stream - 11

Table C-3

RESULTS OF SLUDGE ENRICHMENT

| Experiment Number | Feed P, ppm | % $P_2O_5$, Calcined Sludge | |
|---|---|---|---|
| | | Before Slaking | After Slaking |
| 1 | 6 | 7.3 | 11.7 |
| 2 | 5 | 5.6 | 9.2 |
| 3 | 15.5 | 18.9 | 23.6 |

## APPENDIX C (cont'd)

### Table C-4

EFFLUENT ANALYSIS FOR EXPERIMENT 3

| | Batch Number (1 liter each) | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | Avg. |
| *Secondary Effluent Analysis | | | | | |
| Ca Hardness (mg/l Ca) | 93.0 | 93.0 | 93.0 | 93.0 | 93.0 |
| Mg Hardness (mg/l Mg) | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 |
| P (mg/l P) | 15.5 | 15.5 | 15.5 | 15.5 | 15.5 |
| Suspended Solids (mg/l) | 49.4 | 49.4 | 49.4 | 49.4 | 49.4 |
| Alkalinity (mg/l $HCO_3^-$) | 119.0 | 119.0 | 119.0 | 119.0 | 119.0 |
| Fresh Water Analysis | | | | | |
| Hardness (mg/l $CaCO_3$) | | | | | 120.0 |
| **Tertiary Effluent Analysis | | | | | |
| Ca Hardness (mg/l Ca) | 24.0 | 20.0 | 38.0 | 69.0 | 38.0 |
| Mg Hardness (mg/l Mg) | 2.0 | 3.0 | 2.0 | 1.0 | 2.0 |
| P (mg/l P) | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| Treatment Data | | | | | |
| pH -- initial | 7.1 | 7.0 | 7.1 | 7.0 | |
| pH - after sludge + CaO | 11.3 | 11.0 | 11.0 | 11.0 | |
| pH - after $CO_2$ | 9.0 | 9.0 | 9.0 | 8.5 | |
| Lime Dose (mg) | 400 | | | | |
| Sludge Recovery (mg) | 444.9 | | | | |
| Make-up Lime (mg) | | 58.4 | | | |
| Sludge Recovery (mg) | | 599.0 | | | |
| Make-up Lime (mg) | | | 1.4 | | |
| Sludge Recovery (mg) | | | 638.4 | | |
| Make-up Lime (mg) | | | | 43.8 | |
| Sludge Recovery (mg) | | | | 741.2 | |
| SLUDGE BUILD-UP (%) (TOTAL RECYCLE) | 0.0 | 34.6 | 42.8 | 66.6 | |
| SLUDGE RECOVERY (mg) (AFTER SLAKING) | | | | 591.8 | |

*Stream 1 Feed
**Stream 11 Effluent

# APPENDIX D

## MATHEMATICAL MODEL EQUATIONS

ASSUMPTIONS

1. Steady - state for $10^6$ gallons
2. 400 mg/ℓ lime dose.
3. All P as $Ca_5OH(PO_4)_3$ in stream 10.
4. 75% suspended solids volatile.
5. CaO solubility = 1.2g/ℓ at 25°C.

VARIABLES

CAI = Ca content of stream 1 in mg/ℓ as Ca*

CAII = Ca content of stream 11 in mg/ℓ as Ca*

AMGI = Mg content of stream 1 in mg/ℓ as Mg

AMGII = Mg content of stream 11 in mg/ℓ as Mg

PI = P content of stream 1 in mg/ℓ as P

PII = P content of stream 11 in mg/l as P

SSOLD = suspended solids content of stream 1 in mg/ℓ

ATTR = attrition factor (from 0 to 1.0, as .95 for 5% loss)

HCO3 = bicarbonate content of stream 1 in mg/ℓ as $HCO_3$

CACO3 = hardness of fresh water water as mg/ℓ $CaCO_3$

SLUDG = sludge build-up allowed (from 0 to 1.0, as 0.25 for 25% build-up).

---

*Stream 1 = Stream one

Stream 11 = Stream eleven

Equation 1

(1) lbs. = Stream 10 $Ca_5OH(PO_4)_3$ weight

= ATTR (PI mg/l - PII mg/l)(8.345 lbs - l/mg - $10^6$ gal) (FW $Ca_5OH(PO_4)_3$/3FW P)

= ATTR (PI-PII)(8.345)(500/91) lbs.

= ATTR (PI-PII)(45.84) lbs.

Equation 2

(2) lbs. = Stream 10 MgO weight

= ATTR (AMGI mg/l - AMGII mg/l)(8.345 lbs - l/mg - $10^6$ gal) (FW MgO/FW Mg)

= ATTR (AMGI - AMGII)(8.345)(40.3/24.3) lbs.

= ATTR (AMGI-AMGII)(13.84) lbs.

Equation 3

(3) lbs. = Stream 10 total weight

= (1) + (2) + ATTR (SSOLD mg/l)(0.25)(8.345 lbs - l/mg - $10^6$ gal)

= (1) + (2) + ATTR (SSOLD)(2.09) lbs.

Equation 4

(4) % = Percent $Ca_5OH(PO_4)_3$ in Stream 10

= [(1)/(3)](100)%

Equation 5

(5) % = Percent $P_2O_5$ in Stream 10

= {[(1)(3·FW $P_2O_5$/2·FW $Ca_5OH(PO_4)_3$)]/(3)} (100)

= [(1)(3·142/2·500)(100)]/(3)

= [(1)(42.6)]/(3)%

Equation 6

(6) lbs. = Weight $CO_2$ added Stream 14 (dependent on free Ca from Streams 1 and 2)

= (8.345 lbs - l/mg - $10^6$ gal)(FW $CO_2$/FW Ca)
[(400)(FW Ca/FW CaO) + (CAI - CAII) - (PI - PII)(5 x FW Ca/3 x FW P) - ($HCO_3$)(FW Ca/FW $HCO_3$)]

= (8.345)(44/40)[(400)(40/56) + (CAI - CAII) - (PI - PII)(5 x 40/3 x 31) - (HCO3)(40/61)]

= (2621.60) + (CAI - CAII)(9.18) - (PI - PII)(19.73) - (HCO3)(6.01) lbs.

Equation 7

(7) lbs. = Weight $CO_2$ given off in Stream 15

= $CO_2$ added Stream 14 + bicarbonate in Stream 1

= (6) + (HCO3)(6.01)

= (2621.60) + (CAI - CAII)(9.18) - (PI - PII)(19.73) lbs.

Equation 8

(8) gal. = Gallons of fresh water for slaking in Stream 8

= Weight of CaO/solubility of CaO corrected for hardness

$$= \frac{(SLUDG)(FW\ CaO/FW\ Ca)\ (7)\ lbs.}{(7.4\times10^{-6}\ lbs\text{-}l/mg\text{-}gal)[857\ mg/l-(CACO3)(FW\ Ca/FW\ CaCO_3)\ mg/l]}$$

$$= \frac{(SLUDG)(56/44)(7)}{(7.4\times10^{-6})[857 - (CACO3)(40/100)]}\ gal.$$

$$= \frac{(SLUDG)[3336.56+(CAI-CAII)(11.68)-(PI-PII)(22.60)]10^6}{6341.80-(CACO3)(2.96)}$$

gal.

Equation 9

$$(9) = \text{Fraction of Stream 9 to Stream 13}$$

$$= \frac{\text{CaO need - CaO in Stream 5}}{\text{CaO in Stream 7 + CaO in fresh water for slaking}}$$

$$= \frac{A-B}{C+D}$$

where A = (400 mg/l)(8.345 lbs - l/mg - $10^6$ gal) = 3338.00 lbs.

B = (1.00 - SLUDG)(FW CaO/FW $CO_2$)(7) lbs.

= (1.00 - SLUDG)(56/44)(7) lbs.

= (1.00 - SLUDG)[(3336.58)+(CAI-CAII)(11.68)-(PI-PII)(22.60)] lbs.

C = (SLUDG)(FW CaO/FW $CO_2$)(7) lbs.

= (SLUDG)(56/44)(7) lbs.

= (SLUDG) [(3336.58)+(CAI-CAII)(11.68)-(PI-PII)(22.60)] lbs.

D = (CACO3 mg/l)(FW CaO/FW $CaCO_3$)(8 gal)($7.4 \times 10^{-6}$ l-lbs/mg-gal)(SLUDG)

= (CACO3)(40/100)(8)($7.4 \times 10^{-6}$) lbs. (SLUDG)

$$= (\text{SLUDG}) \left[\frac{(\text{CACO3})\{(2469.05)+(\text{CAI-CAII})(8.64)-(\text{PI-PII})(16.72)\}}{(1585.45) - (\text{CACO3})(0.74)}\right] \text{ lbs.}$$

Equation 10

(10) lbs. = Weight of $CO_2$ added Stream 16

= [(8) gal][1.00 - (9)] ($6341.8 \times 10^{-6}$ lbs/gal)(FW $CO_2$/FW CaO)

= [(8)][1.00-(9)][($6341.8 \times 10^{-6}$)(44/56)]

= [(8)][1.00-(9)][$4975.71 \times 10^{-6}$] lbs.

Equation 11

*(11)* lbs. = Weight of $CaCO_3$ recovered in Stream 12
= [*(10)*] (FW $CaCO_3$/FW $CO_2$) lbs. (ATTR)
= [*(10)*] (100/44) (ATTR)
= [*(10)*] (2.27) lbs. (ATTR)
= (ATTR) (2.27) [*(10)*] lbs.

Equation 12

*(12)* gal. = Gallons of water recovered in Stream 17
= [*(8)*] [1.00-*(9)*] gal.

Equation 13

*(13)* lbs. = Weight of CaO make-up in Stream 6 (equal to zero when answer (9) is 1.00 or less)
= CaO need - CaO from Streams 5 and 13
= (400 mg/1)(8.345 lb-l/mg-$10^6$ gal) - [*(7)*] (FW CaO/FW $CO_2$)
= 3338.00 - [*(7)*] (56/44)
= (PI-PII)(22.64) - (CAI-CAII)(11.70) - 3.35 lbs.

Equation 14

*(14)* = Make-up lime dose to total lime dose ratio
= *(13)*/3338.00

X = cycle number from 1 through 10

$K_X$ = weight in lbs of Stream 4 after X cycles with total recycle

$L_X$ = percent sludge weight build-up in Stream 4 after X cycles using cycle 1 weight as reference (0%)

$$K_X = (ATTR)\,[X\{(SSOLD)(0.25)\ mg/l\ (8.345\ lb\text{-}l/mg\text{-}10^6\ gal) + (AMGI\text{-}AMGII\ mg/l)(8.345\ lb\text{-}l/mg\text{-}10^6\ gal)(FW\ MgO/FW\ Mg) + (PI\text{-}PII\ mg/l)(8.345\ lb\text{-}l/mg\text{-}10^6\ gal)(FW\ Ca_2P_2O_7/2\ FW\ P) + (CAI\text{-}CAII)(8.345\ lb\text{-}l/mg\text{-}10^6\ gal)(FW\ CaO/FW\ Ca) - (PI\text{-}PII)(mg/l)(8.345\ lb\text{-}l/mg\text{-}10^6\ gal)(2\ FW\ CaO/2\ FW\ P)\} + (400\ mg/l)(8.345\ lb\text{-}l/mg\text{-}10^6\ gal)]$$

where

$FW\ MgO = 40.3$

$FW\ Mg = 24.3$

$FW\ Ca_2P_2O_7 = 254$

$FW\ P = 31$

$FW\ CaO = 56$

$FW\ Ca = 40$

$$K_X = (ATTR)\,[X\{(SSOLD)(2.09) + (AMGI\text{-}AMGII)(13.84) + (PI\text{-}PII)(34.19) + (CAI\text{-}CAII)(11.68) - (PI\text{-}PII)(15.07)\} + 3338]\ lbs.$$

$$L_X = \left(\frac{K_X}{K_1} - 1.00\right)(100)\%$$

For X = 1 through 10 calculate all $K_X$ and $L_X$ values.

# APPENDIX E

## MATHEMATICAL MODEL PROGRAM

```
$NIBECXLROUTINE
*IOCS(CARD,1132 PRINTER,DISK)
*ONE WORD INTEGERS
C
C      CAI = CA CONTENT OF STREAM  1 IN MG/L AS CA
C
C      CAII = CA CONTENT OF STREAM 11 IN MG/L AS CA
C
C      AMGI = MG CONTENT OF STREAM  1 IN MG/L AS MG
C
C      AMGII = MG CONTENT OF STREAM 11 IN MG/L AS MG
C
C      PI =  P CONTENT OF STREAM  .  .. MG/L AS P
C
C      PII =  P CONTENT OF STREAM 11 IN MG/L AS P
C
C      SSOLD = SUSPENDED SOLIDS CONTENT OF STREAM 1 (MG/L).
C
C      ATTR = ATTRITION FACTOR (FROM 0 TO 1    .95 FOR 5 PERCENT LOSS,
C                                              .92 FOR 8 PERCENT LOSS ETC)
C
C      HCO3 = BICARBONATE CONTENT OF STREAM 1 AS HCO3- (MG/L).
C
C      CACO3    = HARDNESS OF FRESH WATER AS  CACO3 MG/L
C
C      SLUDG    = SLUDGE BUILD-UP ALLOWED EXPRESSED FROM 0 TO 1.0
C                 ( 0.25 FOR 25 PERCENT , 0.50 FOR 50 PERCENT , ETC.)
C
      DIMENSION ISTAR(60)
      DATA ISTAR/60*'**'/
  100 FORMAT(6F10.0)
  200 FORMAT(1H ,T11,'CYCLE NUMBER',84,I2,6X,'KX',F20.2,8X,'LX',F20.2)
  210 FORMAT(1H1,T51,'INPUT VARIABLES')
  215 FORMAT(1H0,T11,'CA CONTENT OF STREAM  I   (MG/L) AS CA',12X,F20.2/
     1T11,'CA CONTENT OF STREAM II   (MG/L) AS CA',12X,F20.2/T11,'MG CON
     2TENT OF STREAM  I   (MG/L) AS MG',12X,F20.2/T11,'MG CONTENT OF STR
     3EAM II   (MG/L) AS MG',12X,F20.2/T11,'P  CONTENT OF STREAM  I   (M
     4G/L) AS  P',12X,F20.2)
  220 FORMAT(T11,'P  CONTENT OF STREAM II   (MG/L) AS  P',12X,F20.2/T11,
     2'SUSPENDED SOLIDS CONTENT OF STREAM I  (MG/L)',6XF20.2/T11, 'ATTRI
     3TION FACTOR',34X,F20.2/T11,'BICARBONATE CONTENT OF STREAM I AS HCO
     43-  (MG/L)',2X,F20.2/T11,'HARDNESS OF FRESH WATER  AS CACO3 (MG/L)
     5',10X,F20.2)
  225 FORMAT(T11,'SLUDGE BUILD-UP ALLOWED (0-1)',21X,F20.2)
  250 FORMAT(1H0,T51,'OUTPUT')
  251 FORMAT(1H0,T11,'PER CENT CA5OH(PO4)3 IN STREAM 10',17X,F20.2,2X,'P
     1ER CENT')
  255 FORMAT(1H ,T11,'CA5OH(PO4)3 IN STREAM 10',26X,F20.2,2X,'LBS.'/T11,
     1'MGO IN STREAM 10',34X,F20.2,2X,'LBS.'/T11,'TOTAL WEIGHT OF STREAM
     2 10',25X,F20.2,2X,'LBS.'/T11,'PERCENT P2O5 IN STREAM 10',25X,F20.2
     4,2X,'PER CENT'/T11,'CO2 IN STREAM 14',34X,F20.2,2X,'LBS.'/T11,'CO2
     3 IN STREAM 15',34X,F20.2,2X,'LBS.')
  260 FORMAT(T11,'FRESH WATER IN STREAM 8',27X,F20.2,2X,'GALLONS'/T11,'F
     1RACTION OF STREAM 9 TO STREAM 13',17X,F20.2,2X          /T11,'CO2
     2 IN STREAM 16',34X,F20.2,2X,'LBS.'/T11,'CACO3 RECOVERED IN STREAM
     412',22X,F20.2,2X,'LBS.'/T11,'FRESH WATER EFFLUENT IN STREAM 17',17
     5X,F20.2,2X,'GALLONS')
  280 FO      ,'STEADY STATE FOR 1 MILLION GALLONS WITH 400 MG/L LIME
     1DOSE  .  STREAM 1'/ ' ASSUMING A. ALL P AS CA5OH(PO4)3 IN STREAM 10
     2'/ '          B.  75 PER CENT SUSPENDED SOLIDS VOLATILE')
  281 FORMAT(1H0,'KX= WEIGHT IN LBS OF STREAM 4 AFTER X CYCLES WITH TOTA
     1L RECYCLE'/' LX= PER CENT SLUDGE WEIGHT BUILD-UP IN STREAM 4 AFTER
     2 X CYCLES WITH TOTAL RECYCLE')
```

```
  300 FORMAT(//,T55,'LBS.',T83,'PER CENT')
  310 FORMAT(/)
  400 FORMAT(60A2)
  410 FORMAT(T11,'CAO MAKE-UP IN STREAM 6',27X,F20.2,2X,'LBS.'/
     1T11,'MAKE-UP CAO DOSE TO TOTAL CAO DOSE RATIO',10X,F20.2)
CC
C
C*****************************************************************
C
C          INPUT SECTION
C
C     ALL INPUT VARIABLES USE FIELD SPECIFICATION
C     6F10.0 IN THE FOLLOWING ORDER
C     CAI       CAII       AMGI       AMGII      PI         PII
C     SSOLD     ATTR       HCO3       CACO3      SLUDG
C
C*****************************************************************
C
C
      READ(2,100)CAI,CAII,AMGI,AMGII,PI,PII,SSOLD,ATTR,HCO3,CACO3,SLUDG
      WRITE(3,210)
      WRITE(3,215) CAI,CAII,AMGI,AMGII,PI
      WRITE(3,220)PII,SSOLD,ATTR,HCO3,CACO3
      WRITE(3,225) SLUDG
C
C     EQ. 1 WGT OF CA5OH(PO4)3 IN STREAM 10
C
      CAPO4    = ATTR*(PI-PII)*45.84
C
C     EQ. 2 WGT OF MGO IN STREAM 10
C
      AMGO     = ATTR*(AMGI-AMGII)*13.84
C
C     EQ. 3 TOTAL WGT IN STREAM 3.
C
      TWGT1    = CAPO4 + AMGO + ATTR*SSOLD*2.09
      PCAPO=(CAPO4/TWGT1)*100.
C
C     EQ. 4PER CENT P2O5 IN STREAM 10.
C
      F1       = (PI - PII)*1952.8
      P2O5     = F1/(((PI - PII)*45.84)+((AMGI-AMGII)*13.84)+SSOLD*2.09
C
C         WGT OF CO2 IN STREAM 14
C
      CO214    = ((2621.6 +(CAI - CAII)*9.18)-((PI-PII)*19.73))-HCO3*5.
C
C     EQ. 6 WGT OF CO2 GIVEN OFF IN STREAM 15
C
      CO215    = (2621.6+(CAI-CAII)*9.18)-(PI-PII)*19.73
C
C     GALLONS OF FRESH WATER FOR SLAKING EQ. 7
C
      H2O8     = SLUDG* ((3336.56+(CAI-CAII)*11.68)-(PI-PII)*22.6)
      H2O8     = (H2O8/(6341.8-CACO3*2.96))*1.E6
C
C     EQ. 8 FRACTION OF STREAM 9 TO STREAM 13
C
      F1       = ((3336.58 + (CAI-CAII)*11.68)-(PI-PII)*22.6)
      F2       = (CACO3*((2469.05+(CAI-CAII)*8.64)-(PI-PII)*16.72
     1))/(1585.45-CACO3*.74)
      FRAC1    = (3338.-(1.-SLUDG)*F1)/(SLUDG*F1+SLUDG*F2)
      IF(FRAC1-1.)55,50,50
   50 FRAC1=1.
C
C     EQ. 9 CO2 IN STREAM 16
```

```
C
   55 CO216   = M2O8*(1.-FRAC1)*4.4/571E-3
C
C     EQ. 10 CACO3 RECOVERED IN STREAM 12
C
      CO317   = CO216*2.27*ATTN
C
C     EQ. 11 FRESH WATER EFF UENT IN STREAM 17
C
      M2017   = M208*(1.-FRAC. )
E
C
C
C          OUT PUT SECTION
C
      IF(FRAC1-1.)60,60,65
   60 CA06=0.
      RAT=0.
      GO TO 70
   65 CA06=3338.-(336*.25+((CAI-CAII)*11.7+((PI-PII)*22.84)))
      RAT=CA06/3338.
   70 CONTINUE
      WRITE(3,310)
      WRITE(3,400)ISTAR
      WRITE(3,280)
      WRITE(3,300)
C     IX       = CYCLE NUMBER 1, 2, 3, ...10
C     AKIX     = WUTLOSS OF STREAM 4 AFTER IX CYCLES WITH TOTAL RECYCLE
C
C     ALX      = PER CENT SLUDGE WEIGHT BUILD-UP IN STREAM 4 AFTER IX CYCLES
C                USING 1 WEIGHT AS REFERENCE TO PER CENT.
C
      F1       = 2.0*SSOLD*(AMG1-AMGII)*13.944*(PI-PII)*94.19*(CAI-CAII)*
     1(1.0**(PI-PII))*1.5E07
      AKIX     = ATTN*(F1+3338.)
      DO 10 IX = 1,10
      AKIX     = ATTN* ((IX*F1+3338.)
      ALX      = (AKIX/AKIX-1.)*100.
      WRITE(3,290) IX,AKIX,ALX
   10 CONTINUE
      WRITE(3,320)
      WRITE(3,400)ISTAR
      WRITE(3,290)
      WRITE(3,250)PCAMG
      WRITE(3,255)CAP04,AMGO,TWGT1,P205,CO216,CO219
      WRITE(3,260) M208, FRAC1, CO216, CO316, M2017
      WRITE(3,410)CA06,RAT
      CALL EXIT
      END
VARIABLE ALLOCATIONS
   CAII  R  0000       CAI   R  0002       AMG1R  R  0006       AMGIIR  R  0008       F1R   R  0004       PIIR  R  0008
  SSOLDR  R  000C       ATTNR  R  000E       PCO3R  R  0010       CACO3R  R  0012       SLUDGR  R  0014       CAPO4R  R  0016
  AMGOR  R  0018       TWGT1R  R  001A       PCAPOR  R  001C       F1R   R  001E       P2O5R  R  0020       CO219R  R  0022
  CO215R  R  0024       M2OBR  R  0026       F2R   R  0028       FRAC1R  R  002A       CO216R  R  002C       CO316R  R  002E
  M2017R  R  0030       CA06R  R  0032       RATR  R  0034       RATIOR  R  0036       AKIR  R  0038       ALR   R  003A
  ISTARII  R  0C7F=0044       IXII  R  0080

STATEMENT ALLOCATIONS
  100  *0006  200  *00C9  210  *00DE  215  *00FB  220  *0165  225  *0108  250  *01EF  251  *01F7  255  *0625  260  *0630
  280  *02FF  281  *0359  300  *034A  310  * 387  400  *0389  410  *038C  50  *0534  55  *0538  60  *053E  65  *0540
  70  *0584  10  *05F4

FEATURES SUPPORTED
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CALLED SUBPROGRAMS
 FSUB    FMPY    FDIV    FLD     FSTD    FSBR    FDVR    FLOAT   CARDZ   PRNTZ   SKED    SKNT    SETUP   SYTU    SETUL
 SIOF    SIOI    SOFTC

REAL CONSTANTS
  .498400E 02+0082      .138400E 02+0084      .626000E 01+0086      .600000E 03+0088      .[illegible]
  .914000E 01+008E      .177600E 02+0090      .601000E 01+0092      .333656E 04+0094      .[illegible]
  .634180E 04+009A      .296000F 01+009C      .100000E 07+009E      .333658E 04+00A0      .[illegible]
  .167200E 02+00A6      .158545E 04+00A8      .740000E 00+00AA      .333200E 04+00AC      .[illegible]
  .227000E 01+00B2      .000000F 00+00B4      .134135E 04+00B6      .117030F 02+00B8      .[illegible]
  .341900E 02+00BE      .150700E 02+00C0

INTEGER CONSTANTS
     2+00C2       3+00C3       1+00C4      10+00C5

CORE REQUIREMENTS FOR
 COMMON       3  VARIABLES    130  PROGRAM   1484

 END OF COMPILATION
```

# APPENDIX F

Cost estimates at this stage in process evolution necessarily involve a number of assumptions. Following are assumptions employed in the preliminary cost estimates presented in this report. Following the assumptions is an example of the various cost elements for Case 1-a.

## MASS BALANCE ASSUMPTIONS

Mass balance data used in the calculations were taken from Table XVIII, page 38. The data refer to 10 ppm of phosphorus in the secondary effluent and 90% removal efficiency. Assumptions were made in the mass balance to determine the wet solid material properties:

- 2.5% solid (97.5% moisture) in the stream from the first thickener (phosphate sludge) and 20% solid (80% moisture) in the same stream after centrifuging.

- 20% solid (80% moisture) in the stream from the second thickener (calcium carbonate sludge) and 85% solid in the same stream after its centrifuging.

## TOTAL INVESTMENT ASSUMPTIONS

Unless noted otherwise, equipment cost data were obtained from the manufacturer or vendor. In the total investment calculations the following assumptions were made:

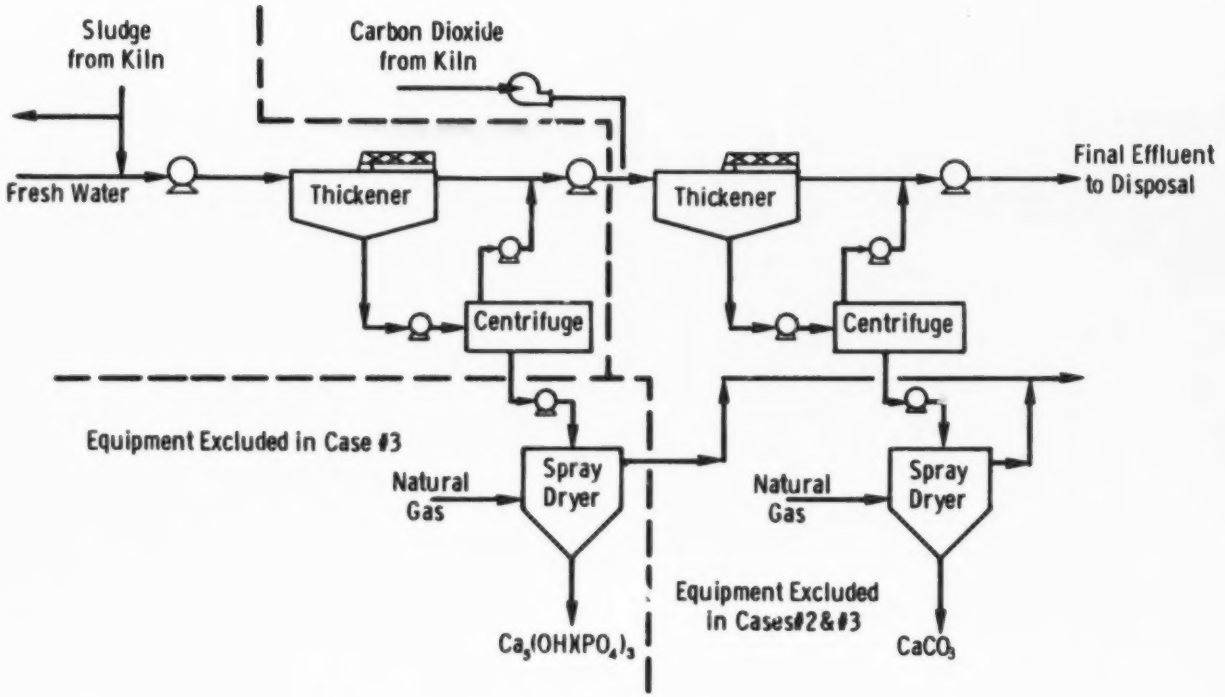


Figure F-1. Preliminary Schematic Flow Diagram for Cost Estimating

| | | |
|---|---|---|
| a) | Purchased equipment installation | |
| | 1. Thickeners | the installation cost of this item is included in cost of the equipment, per the manufacturer. |
| | 2. Dumps | 30% of the purchased equipment cost. |
| | 3. Centrifuges | 35% of the purchased equipment cost. |
| | 4. Dryers | 100% of the purchased equipment cost. |
| | 5. Blowers | 50% of the purchased equipment cost. |
| | 6. Electric Motors | 50% of the purchased equipment cost. |
| b) | Piping | 30% of the purchased equipment cost. |
| c) | Instrumentation | 13% of the purchased equipment cost. |
| d) | Electrical | 10% of the purchased equipment cost. |
| e) | Building | 7% of the purchased equipment cost. |
| f) | Land and Yard Improvements | 15% of the purchased equipment cost |
| g) | Utilities | 30% of the purchased equipment cost. |
| h) | Engineering and Construction | 30% of the physical plant cost if that is less than $\$1 \times 10^6$ |
| | | 25% of the physical plant cost if that is more than $\$5 \times 10^6$ and less than $\$1 \times 10^6$ |
| i) | Contingency and Contractor's Fee | 20% of the direct plant cost. |

OPERATING COST

The assumptions made in calculating operating costs were:

a. Cost of the electricity - \$0.018/kwhr
b. Cost of the natural gas - \$0.65/1000 SCF
c. Labor cost - \$3.00/man-hr
d. Number of operators per shift.

APPENDIX F (cont'd)

SUMMARY

CAPITAL COST ESTIMATE

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^6$ GPD

Case: 1

| | | Cost - $ | % of Total |
|---|---|---|---|
| 1. | Purchased Equipment | 46,450 | 21.98 |
| 2. | Purchased Equipment Installation | 28,300 | 13.39 |
| 3. | Piping | 13,900 | 6.58 |
| 4. | Instruments | 6,000 | 2.84 |
| 5. | Insulation | --- | --- |
| 6. | Electrical | 4,650 | 2.20 |
| 7. | Building | 3,250 | 1.54 |
| 8. | Land & Yard Improvements | 6,950 | 3.29 |
| 9. | Utilities | 13,900 | 6.58 |
| 10. | Physical Plant Cost | 123,400 | 58.40 |
| 11. | Engineering and Construction | 37,000 | 17.51 |
| 12. | Direct Plant Cost | 160,400 | 75.91 |
| 13. | Contingency & Contractor's Fee | 32,100 | 15.19 |
| 14. | Fixed Capital Cost | 192,500 | 91.10 |
| 15. | Working Capital | 18,800 | 8.90 |
| | TOTAL INVESTMENT | 211,300 | 100.00 |
| 16. | Capital Requirements $/GPD 0.211 | | |

APPENDIX F (cont'd)

SUMMARY

ANNUAL OPERATING COST ESTIMATE

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^6$ GPD

Case: 1

Fixed Capital Cost: $192,500

| | Item | Total $ | % |
|---|---|---|---|
| 1. | Raw Materials and Chemicals | --- | --- |
| 2. | Direct Labor | 27,000 | 29.82 |
| 3. | Supervision | --- | --- |
| 4. | Maintenance, 5% of Fixed Capital | 9,650 | 10.66 |
| 5. | Supplies, 15% of Maintenance | 1,450 | 1.60 |
| 6. | Utilities | 1,260 | 1.39 |
| 7. | Other | 1,720 | 1.90 |
| 8. | Total Direct Cost | 41,080 | 45.37 |
| 9. | Payroll Burden, 20% of 2 and 3 | 5,400 | 5.96 |
| 10. | Plant Overhead, 50% of 2, 3, 4, and 5 | 19,050 | 21.04 |
| 11. | Pack and Ship | --- | --- |
| 12. | Waste Disposal | --- | --- |
| 13. | Other | --- | --- |
| 14. | Total Indirect Cost | 24,450 | 27.00 |
| 15. | Depreciation, 10% Fixed Capital/Yr | 19,250 | 21.26 |
| 16. | Taxes, 2% of Fixed Capital | 3,850 | 4.25 |
| 17. | Insurance, 1% of Fixed Capital | 1,920 | 2.12 |
| 18. | Other | --- | --- |
| 19. | Total Fixed Cost | 25,020 | 27.63 |
| 20. | Total Operating Cost | 90,550 | 100.00 |
| 21. | Cost: $/M Gal 0.28 | | |
| 22. | By-Product Credit | | |
| 23. | Adjusted Operating Cost | | |
| 24. | Adjusted Cost: $/GPD | | |

## SUMMARY

## PURCHASED-EQUIPMENT COST

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^6$ GPD

Case: 1

| | Cost-$ | PerCent |
|---|---|---|
| 1) Thickeners, 2 | 13,300 | 28.63 |
| 2) Pumps and motors, 9 ea. | 3,800 | 8.18 |
| 3) Centrifuges, 2 | 11,600 | 24.97 |
| 4) Spray dryers, 2 | 17,425 | 37.51 |
| 5) Blower and motor, 1 ea. | 325 | 0.71 |
| TOTAL COST | 46,450 | 100.00 |

APPENDIX F (cont'd)

SUMMARY

PURCHASED-EQUIPMENT INSTALLATION COST

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^6$ GPD

Case: 1

| | Cost-$ | Per Cent |
|---|---|---|
| 1) Thickeners | 4,650 | 16.43 |
| 2) Pumps and motors | 1,880 | 6.64 |
| 3) Centrifuges | 4,150 | 14.66 |
| 4) Spray dryers | 17,460 | 61.70 |
| 5) Blower and motor | 160 | 0.57 |
| TOTAL COST | 28,300 | 100.00 |

APPENDIX F (cont'd)

SUMMARY

WORKING CAPITAL ESTIMATE

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^6$ GPD

Case: 1

| | | Cost - $ | % |
|---|---|---|---|
| 1. | Raw Material and Chemicals Inventory | --- | --- |
| 2. | Direct Labor | 7,960 | 42.34 |
| 3. | Indirect Cost | 6,110 | 32.50 |
| 4. | Operating Supplies | 360 | 1.91 |
| 5. | Fixed Cost | 1,440 | 7.66 |
| 6. | Spare Parts | 1,210 | 6.44 |
| 7. | Miscellaneous, 10% of 1 to 6 | 1,720 | 9.15 |
| | Total | 18,800 | 100.00 |

Number of operators per shift: one

# APPENDIX G

## COMBINED SYSTEMS COST DETAILS

### MASS BALANCE ASSUMPTIONS

Mass balances for the various cases were calculated with the aid of all available data (Recovery of Coagulant, Nitrogen Removal, and Carbon Regeneration in Waste Water Reclamation, Final Report of Project Operations, Department of Interior, FWPCA, Grant WPD-85. June 1967; Public Works for December, 1968, p. 6; Memo from J. B. Farrell to Dr. R. B. Dean, March 6, 1969; Nutrient Removal at Lake Tahoe, Costs and Criteria, L. G. Suhr). However, it was also necessary to make a number of assumptions as follows:

- solid material leaving the furnace contains 67.11% Ca and 2.66% P (analysis made at MRC)
- solubility of lime was assumed 1.0 g $Ca(OH)_2$/l at conditions
- 2% solid (98% moisture) in the stream from the phosphate sludge thickener and 20% solid (80% moisture) after stream centrifugation
- 20% solid (80% moisture) in the stream from the second calcium carbonate thickener and 85% solid (15% moisture) after stream centrifugation
- carbonation will be done by means of flue gas from the calciners or sludge incinerators with $CO_2$ content 10%
- $CO_2$ absorption efficiency 50%
- double flue gas volume increase because of its temperature expansion
- complete phosphate removal in the form $Ca_5(OH)(PO_4)_3$ from the phosphate sludge thickener
- complete lime carbonation and removal from calcium carbonate thickener

TOTAL INVESTMENT ASSUMPTIONS

In making total investment calculations the following assumptions were made:

(a) Purchased-equipment installation

| Equipment Item | % of Purchased-equipment cost |
|---|---|
| Hopper | 4 |
| Mixer | 62 |
| Pumps | 140 |
| Blower | 60 |
| Centrifuge | 60 |
| Furnace | 50 |
| Dryer | 74 |

- the installation cost of thickeners was discussed with the manufacturer

- the installation cost of flocculators was assumed as 40% of that for thickeners of the same size

(b) Piping - 30% of the purchased-equipment total cost

(c) Instrumentation - 13% of the purchased-equipment total cost

(d) Insulation - 8% of the purchased-equipment total cost (in the first case not cost for insulation was assumed)

(e) Electrical - 10% of the purchased-equipment total cost

(f) Building - 7% of the purchased-equipment total cost

(g) Land and Yard Improvements - 15% of the purchased-equipment total cost

(h) Utilities - 30% of the purchased-equipment total cost (in the first case no cost for utilities was assumed)

(i) Engineering and Construction

- 30% of the physical-plant cost if that is less than $10^6$

- 25% of the physical-plant cost if that is less than $\$5 \times 10^6$ and more than $\$10^6$

- 20% of the physical-plant cost if that is more than $\$5 \times 10^6$

(j) Contingency and Contractor's Fee

- 20% of the direct-plant cost

OPERATING COST

The assumptions made for this item are as follows:

- the cost of electricity was taken ¢0.6/k hr
- the cost of natural gas was taken ¢50/1,000 cuft
- the cost of steam was taken ¢50/1,000 lb
- the cost of lime was taken $15.50/ton
- the cost of one man-hr was taken $3.00/man-hr

Other assumptions are shown as percentages on the operating cost estimate summary sheet example.

EXAMPLE OF COST CALCULATION

One example of the cost calculation is shown, namely, that for Case 5 at a 10-million-gallon-per-day rate. Costs for all five cases at 1-, 10-, and 100-million gallons per day are summarized in Table 27.

PURCHASED-EQUIPMENT COST

| | | $ | % |
|---|---|---|---|
| (1) | Hoppers | 450 | 0.08 |
| (2) | Mixers | 1,370 | 0.23 |
| (3) | Flocculation Basins | 8,800 | 1.50 |
| (4) | Clarifiers | 107,300 | 18.27 |
| (5) | Pumps | 18,530 | 3.15 |
| (6) | Blowers | 10,560 | 1.80 |
| (7) | Centrifuges | 79,740 | 13.58 |
| (8) | Kilns | 345,000 | 58.74 |
| (9) | Dryer | 15,600 | 2.65 |
| | | 587,350 | 100.00 |

APPENDIX G (cont'd)

## CAPITAL COST ESTIMATE SUMMARY

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^7$ GPD

Case: 5

| | | Cost - $ | % of Total |
|---|---|---|---|
| 1. | Purchased Equipment | 587,350 | 23.52 |
| 2. | Purchased Equipment Installation | 296,140 | 11.86 |
| 3. | Piping | 176,000 | 7.05 |
| 4. | Instruments | 76,300 | 3.06 |
| 5. | Insulation | 47,000 | 1.88 |
| 6. | Electrical | 58,710 | 2.35 |
| 7. | Building | 41,100 | 1.65 |
| 8. | Land & Yard Improvements | 88,000 | 3.52 |
| 9. | Utilities | 176,000 | 7.05 |
| 10. | | | |
| 11. | | | |
| 12. | | | |
| 13. | | | |
| 14. | Physical-Plant Cost | 1,546,600 | 61.94 |
| 15. | Engineering and Construction | 386,700 | 15.48 |
| 16. | Direct Plant Cost | 1,933,300 | 77.42 |
| 17. | Contingency & Contractor's Fee | 386,700 | 15.49 |
| 18. | Fixed Capital Cost | 2,320,000 | 92.91 |
| 19. | | | |
| 20. | Working Capital | 177,100 | 7.09 |
| | TOTAL INVESTMENT | 2,497,100 | 100.00 |
| 21. | Capital Requirements | | |
| | $/1000 GPD 250 | | |

APPENDIX G (cont'd)

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year 100% Capacity

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^7$ GPD

Case: 5

Fixed Capital Cost 2,320,000

| | ITEM | TOTAL $ | PER CENT |
|---|---|---|---|
| 1. | Raw Materials & Chemicals | 24,800 | 3.47 |
| 2. | Direct Labor | 78,900 | 11.03 |
| 3. | Supervision | | |
| 4. | Maintenance, 5% of Fixed Capital | 116,000 | 16.22 |
| 5. | Supplies, 15% of Maintenance | 17,400 | 2.43 |
| 6. | Utilities | 54,600 | 7.63 |
| 7. | Other | | |
| 8. | TOTAL DIRECT COST | 291,700 | 40.78 |
| 9. | Payroll Burden, 20% of 2 & 3 | 15,780 | 2.21 |
| 10. | Plant Overhead, 50% of 2, 3, 4 and 5 | 106,150 | 14.84 |
| 11. | Pack & Ship | | |
| 12. | Waste Disposal | | |
| 13. | Other | | |
| 14. | TOTAL INDIRECT COST | 121,930 | 17.05 |
| 15. | Depreciation, 10 % Fixed Capital/Yr. | 232,000 | 32.44 |
| 16. | Taxes, 2% of Fixed Capital | 46,400 | 6.49 |
| 17. | Insurance, 1% of Fixed Capital | 23,200 | 3.24 |
| 18. | Other | | |
| 19. | TOTAL FIXED COST | 301,600 | 42.17 |
| 20. | TOTAL OPERATING COST | 715,230 | 100.00 |
| 21. | COST: ¢/1000 GPD 0.2167 | | |
| 22. | BY-PRODUCT CREDIT | | |
| 23. | ADJUSTED OPERATING COST | | |
| 24. | ADJUSTED COST: $/GPD | | |

## WORKING CAPITAL ESTIMATE SUMMARY

Name of Process: Modified Thermal Beneficiation

Flow Rate: $10^7$ GPD

Case: 5

| | | Cost - $ | Per Cent |
|---|---|---|---|
| 1. | Raw Material and Chemicals Inventory | 2,070 | 1.17 |
| 2. | Direct Labor | 34,225 | 19.33 |
| 3. | Indirect Cost | 30,482 | 17.21 |
| 4. | Operating Supplied | 4,350 | 2.46 |
| 5. | Fixed Cost | 75,400 | 42.57 |
| 6. | Spare Parts | 14,500 | 8.19 |
| 7. | Miscellaneous, 10% of 1 to 6 | 16,073 | 9.07 |
| | TOTAL | 177,100 | 100.00 |

Number of Operators per shift: 3

# APPENDIX H

## TRANSPORTATION COSTS FOR SLUDGE DISPOSAL

Almost all sewage treatment plants can be considered continuous sludge producers. In some areas, particularly those which are highly agricultural, the sludges can be used as soil conditioners and fertilizer but in most cases sludge disposal and/or utilization is becoming a problem.

At any rate, dumping sludge at the treatment plant is no longer a desirable solution and transportation of sludges away from the treatment plant will, sooner or later, play a more important role in lieu of treatment processes that obviate sludge production.

Trucks, railroads, barges and pipelines are considered as means of sludge transportation. Air transportation for this purpose is not considered now or in the foreseeable future.

Obviously, the transportation cost will depend on the location of the treatment plant, shipping distance and sludge characteristics such as density, moisture, etc.

It is anticipated that the cost for sludge transportation, ultimately, will not be essentially different from standard shipping rates. By expressing the cost rates in terms such as $/mile or $/ton-mile, we avoid the sludge characteristics-cost relations.

Figure 1 shows the standard freight rates for shipping of bulk materials. There is seen to be considerable spread in costs. As a matter of fact, actual freight rates are negotiated between the shipper and carrier and involve many factors, e.g., minimum annual through-puts, unit train rates, five-car rates, intermodal competition, etc. Moreover, there are other factors that can affect the actual rates, for example, tax regulations that are essentially influenced by the Federal Government.

For comparison we show the average transit times for chemicals, for example, and the cost of transportation equipment in Tables 1 and 2.

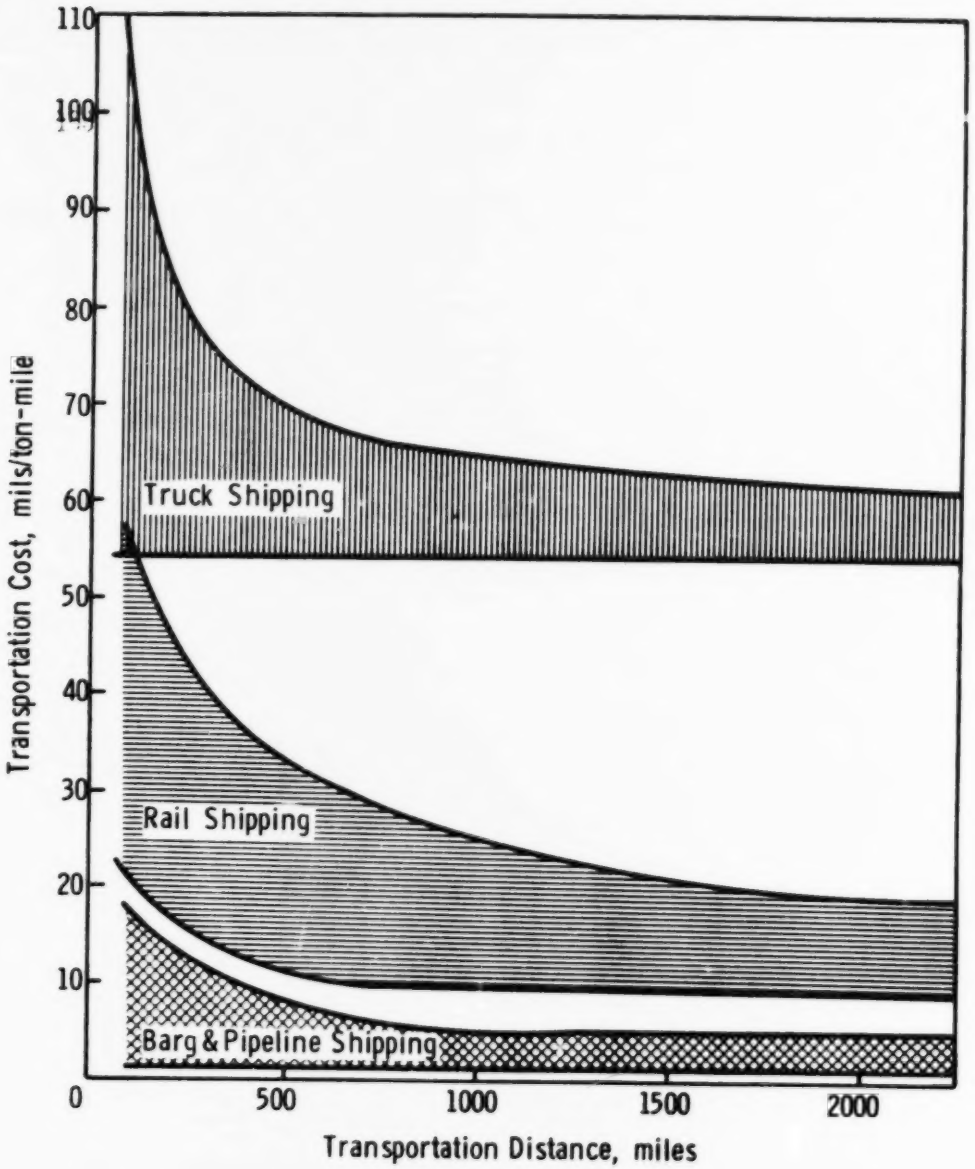


Figure H-1. Shipping Costs for Various Modes of Transportation

Table H-1

AVERAGE TRANSIT TIMES FOR CHEMICALS

| Method | Miles/Day |
|---|---|
| Pipelines | 65 |
| Barge | 100 |
| Rail | 200 |
| Ship tanker | 300 |
| Truck | 700 |

Table 2

COST OF TRANSPORTATION EQUIPMENT*

| | |
|---|---|
| Railway Tank Cars (8,000 gal) | |
| Steel | $13,400 |
| Aluminum | 19,500 |
| Stainless Steel | 32,900 |
| Tractors | |
| Gasoline | 13,500 |
| Diesel | 29,500 |
| Tank Trailers | |
| Carbon Steel | 15,900 |
| Aluminum | 23,200 |
| Stainless Steel | 39,300 |

*Time base: End-1969